COLLOID CHEMISTRY

THEORETICAL AND APPLIED

BY SELECTED INTERNATIONAL CONTRIBUTORS

COLLECTED AND EDITED BY

JEROME ALEXANDER

VOLUME III

FIRST SERIES OF PAPERS ON

TECHNOLOGICAL APPLICATIONS

BOOK DEPARTMENT

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Preface

An ordinary house-fly, if placed within a hollow clear glass globe having a single hole for an outlet, generally escapes rather promptly. But a bee, under like circumstances, seldom escapes. This, as M. Maurice Maeterlinck observed, does not indicate superior wisdom on the part of the fly—quite the contrary. For the fly, dashing hither and thither in planless flight, chances upon the exit, whereas the bee, flying steadfastly towards the light, continues to try to force its way through what must seem to it to be queerly resistant atmosphere. But if we investigate the bee in its hive and enjoy the honey it produces, we will have no doubt as to which is the more advanced and useful insect.

Scientists are not always successful; but like the bee, they are guided by principles and purposes which become more and more intelligent and definite as their wisdom increases with the years. And from the painstaking toil of scientists, citizens at large, be they consumers or stockholders, enjoy far more than honey. On the other hand, as we look with scientifically improved vision into the present and the past, even into the distant "unscientific" past, we are struck by the vast and basic wisdom which has been discovered, preserved, and improved upon by people who never had what we call the advantages of a scientific education. Judgment based on results shows that it is unwise to take a supercilious attitude toward "rule-of-thumb" methods.

Charles Lamb may not have been precisely right about the origin of roast pig; but something of the kind undoubtedly did occur, and we have a much closer and similar story of the discovery of "British gum" (out of which developed later the dextrin which now gums our envelopes and postage stamps), by the observation of a workman that some starch, "torrefied" in a warehouse fire, made a sticky mass with the water used to put the fire out. The Chinese are said to have discovered paper by observing paper-wasps, and printing from the practice of making "rubbed" copies of intaglio-engraved proverbs at shrines, leading later to substitution of carved-in-relief and inked wooden blocks. But when these products and ideas, coming probably via Samarkand, Persia, Arabia, and the Near East, finally reached a scientifically developing Europe, they blossomed into the most potent single aid to civilization, the modern printing press.

There is a wealth of wisdom in "cooking recipes," despite the fact that this term is sometimes used as an acme of scientific scorn. Time out of mind cooks have beaten the whites of eggs separately from the yolks, and secured light cake by carefully folding in the beaten leavening froth of the whites into the batter containing the yolks. The modern physical chemist finds that the

lipoid or fatty matter in the yolks makes the foam bubbles of the beaten whole egg so unstable that if you beat up the whole egg "your cake is all dough." Furthermore, the use of oils or fats as "foam-killers" has long been "rule-of-thumb" practice in many industries, and has also been frequently made use of by sea-captains. In fact, "to throw oil on the troubled waters" has become proverbial.

The upshot of these remarks is that scientists must consider the existence of a long-standing practice as presumptive evidence that there is *something* valuable in or about it, and that exploration in that neighborhood, with impartial separation of gangue, should yield some nuggets of truth. Geologists frequently learn a great deal about the strata of certain regions by a careful examination of mineral grains in ant hills.

All knowledge being founded on experiment and observation, we must never forget that the so-called "Laws of Nature" are not scientific legislation, but represent merely inductive attempts on the part of scientists to combine and coördinate the results of experience in words, graphs or formulas which express what Nature may be expected to do, providing we choose conditions within the limits under which the laws were developed, and avoid the entrance of new factors, an ever-present danger. Extrapolation is often hazardous. While practical masons erect buildings on the assumption that plumb-lines are parallel, plumb-lines in New York and Istanbul are about at right angles to each other.

The increasing recognition of the inevitable ultimate value of research in industry augurs well for the future. Sir William Crookes' warning regarding the danger of nitrogen starvation was answered by science with synthetic nitrates in such quantity that the Chilean industry had to call on scientific surgery to save its very life. Much to be feared is the "text-book" mind, which is foredoomed to confine science to squirrel-cage circles, and industry to dry rot and defeat. About the middle of last century the writer of an authoritative text-book on the steam engine stated in his preface that the current edition would be the last, because everything about steam engines had been worked out and there would be no need of a revised edition. And at that time the Corliss engine was still to be invented!

Probably one of the main defects in modern mass-education with its "yes or no" methods of "examination," is failure to teach that self-respecting humility which keeps the mind open to recognize and accept unprinted and untaught truths. Inevitably, as we enlarge the circle of our experience, we correspondingly enlarge the circle of our ignorance.

It is with mingled feelings of satisfaction and regret that the Editor issues the third and fourth volumes of this series—satisfaction at having been fortunate enough to have secured the splendid coöperation of so many, so able, and so diverse a group of international collaborators, regret at the limitations of time and space which made it impossible to produce books more detailed and ex-

tensive. For example, in lieu of an expected contribution, the Editor received, just prior to going to press, a three hundred page book inscribed by its authors: "You started our writing this book." Nevertheless, the four volumes of this series contain a vast store of varied and ordered information which should render them of great service to seekers after truth in practically all fields of pure and applied science.

As to the arrangement of papers in Vols. III and IV, which conclude the series, the first group consists of subjects of interest to many industries, and comprises eleven papers on *general principles* and six papers dealing with *mechanical* or more specialized matters. The large second group (twenty-five papers) may, for want of a better name, be termed *telluric;* for it deals with matters which are of the earth, earthy, beginning with geology and mineralogy, and running to metals, petroleum, asphalt and agriculture. Vol. IV begins with the third group (fourteen papers) which comprises the very important *carbohydrates,* wood, paper, cellulose, sugar, etc., and also includes dyeing and explosives. The fourth group (thirteen papers) deals with *plastics,* and includes casein, rubber, synthetic resins, tanning and photography. The fifth group (six papers) includes *coatings* such as paints and electrodeposited metals. The sixth group (eight papers) deals with matters of interest in the *ménage,* and has valuable information about washing, baking, butter, brewing, pectin, etc.

It must be emphasized that although Vol. I deals primarily with Theory and Methods, Vol. II with Biology and Medicine, and Vols. III and IV with Technological Applications, Nature pays no attention to the classifications we make for our own convenience. Facts, principles and ideas of technological importance are scattered throughout Vols. I and II. The Editor has in many cases given references of this kind in footnotes. The indexes will disclose many others, for they have been given especial care, with a full realization that extensive indexes are of vital importance in books of this character.

The Editor gratefully acknowledges the aid of many friends who have favored him with criticism, advice and suggestions. Throughout the series full credit has been given, in the proper places, to those who have been aidful in the arduous and sometimes difficult task of making translations, which, in nearly all cases, have been read and checked by the original contributors as well as by the Editor. Thanks are also due to the publisher, the printer and their able assistants for sympathetic and painstaking coöperation in producing a series of books which includes the motley nomenclature and mathematical jargon of so many diverse branches of science, all contributing as fragments to make the extensive mosaic or jig-saw picture of nature and natural phenomena formed by these four volumes on colloid chemistry.

JEROME ALEXANDER.

July 7, 1931.

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Cohesion and Adhesion

By James W. McBain,
Leland Stanford University,

and

Jerome Alexander,
New York.

Adhesion, as a physical property, is defined * as "a molecular force, or the result of it, by which certain bodies stick together." *Cohesion* is defined * thus: "That force by which molecules of the same kind or of the same body are held together, so that the body resists being pulled to pieces. It is strong in solids, weak in liquids, and probably absent in gases. The distinction between *cohesion* and *adhesion,* once insisted upon strongly, is not now regarded as fundamental. Some physicists have limited *cohesion* to particles of the same kind, others to those of the same body. Thus the force that holds the mica to the feldspar in granite would be called *cohesion* by some, and *adhesion* by others."

Prof. C. H. Desch[1] in his introductory paper to the Faraday Society's Symposium on Cohesion, said:

> "For practical purposes it is convenient to distinguish cohesion between atoms, molecules, or ions within a mass of solid or liquids, from the adhesion of one solid to another, or of a liquid to a solid, but there is no theoretical distinction of any importance between the two." And after considering the work of Hardy and Nottage[2] showing that adhesion between solids and liquids depends on the nature of both substances; of McBain and Lee[3] showing that pure chemical individuals in thin films may make powerful adhesives; and of E. A. Ollard[4] showing that an electrodeposited nicked film may in part tear away a steel surface, Desch concludes: 'Such facts show that cohesion and adhesion are fundamentally the same."

The wide use of *adhesives,* such as glues, gums, pastes, etc., has given to *adhesion* the flavor of indicating that two material surfaces are held together through the mediation of a third substance, the adhesive. *Cohesion* indicates rather the inherent strength of a substance, or else that two naked surfaces have stuck together. These surfaces may be of like composition as in the well-known regelation of ice, or they may be dissimilar, as when two different metals are welded together. In processes of this kind it is the outermost efficient surface which counts. Thus if a wood surface have a complete coherent coat of wax or of varnish, it is this outer coat which figures in

* Standard Dictionary. It would be better to say of cohesion: "it *eludes measurement* in liquids, and is *negligible* in gases." For the reasons given by McBain and Lee (*Proc. Roy. Soc.* (*London*), A113, 617 (1927)) cohesion in liquids must be even stronger than it is in solids, but, because of the flow of liquids, is more difficult to demonstrate and measure. Thus the internal pressure of water is 14,000 atmospheres, which indicates great cohesion. In gases the attractive or cohesive forces between like molecules are measured by the van der Waal's constant *a;* and it is interesting to note that from the average magnitude of *a* for gases, and the way in which the effect varies with closeness of contact of the molecules ($\frac{a}{v_2}$), one can approximately predict the tensile strength of steel.

adhesion or cohesion. Frequently the outer surface is invisible, as in the case of mica; two freshly sundered laminations will cohere rather strongly if instantly pressed together, but they speedily lose this property, probably because of adsorption of atmospheric constituents or possibly because of molecular rearrangement at the newly made surfaces. The formation of a new surface skin may be almost instantaneous as in the case of cast iron reported by P. W. Bridgman.[5] A piece of cast iron broken above a vessel of mercury and promptly dropped in, would not amalgamate at the fresh surfaces; but it did amalgamate if broken *under* the mercury.*

The difficulty of obtaining and maintaining clean surfaces is well brought out by Sir Wm. B. Hardy in his paper on "Lubrication" in Vol. I of this series. With surfaces, as in fact with most commercial materials, we are not as a rule dealing with ideal structures as seen in our mind's eye, but rather with *mixtures* as whimsical Dame Nature presents them, or as we may have been able to purify or to separate them. Vanadium is reported in text-books as being brittle; yet Marden and Rich[6] made a highly purified product and found it so malleable that they drew fine wires from it. There is an increasing realization of the importance of "impurities."[7]

Recently the investigations of the structure of matter with the X-ray spectrometer have revealed the existence of super-molecular but sub-microscopic arrangements or *unit cells*,† as they are technically known. With quartz the unit cell appears to consist of three SiO_2 molecules (Bragg) and the cellulose unit cell seems to contain four glucose molecules or residues, forming a so-called crystal unit of cellulose. Unit cells may build up groups of a higher order of magnitude. Thus Mark[8] reports that in cellulose "micelles" are formed by linking together 25 to 30 long molecular chains, each composed of 50 to 100 glucose radicals. As molecules or larger groups of any substance strive towards their final space lattice, foreign molecules or impurities *tend* to become segregated in the interfaces between the crystals. As von Weimarn puts it, crystals *tend* to purify themselves. The great influence of minute percentages of foreign molecules on cohesion and adhesion, thus becomes more understandable.

Some other disturbing features in surfaces are brought out by an experiment of Devaux,[9] who floated a lens-shaped drop of a fluid fatty acid on hot water, and allowed it to chill there. After careful drying, the lower surface could be wet by water, while the upper surface could not. The phenomenon is explainable by the difference in the orientation of the molecules of the fatty acid in the two surfaces of the lens, one of which had set in contact with air, while the other had set in contact with water. In the former case the "oily," hydrocarbon, hydrophobe ends were outwardly directed, whereas in the latter the "watery," COOH, hydrophile ends pointed outward. Analogous differences exist in the various surfaces of crystals, the effect of colloids on crystallization being understandable by preferential adsorption at certain crystal surfaces where crystal growth is inhibited, the other crystal surfaces growing at a disproportionately high rate. We must conclude, therefore, that even with the same chemical composition, the ***structure of the surface*** is a factor to be reckoned with. An interesting research would be to determine the variations in cohesion and in adhesion

* The importance of clean surfaces in soldering is obvious, and "assistants" are used to cleanse the metals being joined, from films of oxide, grease, etc. In galvanizing and electroplating, pickling or abrasive treatment is used to get clean surfaces. In lead-burning, traces of arsenic in the hydrogen or other gas used may be ruinous because of formation of a film of lead arsenide.

† In some cases, unit cells are putative, e.g., with sodium chloride. But especially with more complex compounds there is evidence that the unit cell has a real physical existence. See paper of G. L. Clark in this volume.

shown by isomers, polymers, and tautomers, and by different surfaces of the same crystal.

These considerations apply to adhesives, as well as to surfaces to be joined. Thus McBain and Lee,[10] in reporting on true chemical compounds as adhesives, state that "recent investigations on X-ray diagrams have shown that the results are greatly affected by the manipulative procedure in placing a single pure solid on a given surface, and that several quite distinct molecular arrangements and dimensions of crystal units may be produced. This is evidently one of the factors in the study of adhesives which has not yet been given sufficient attention, and phenomena of this sort may explain some of the hitherto uncontrollable variations in testing joint strength."

"Calcite and some other crystals, when freshly split, have the power of orienting the molecules of isomorphous salts, deposited on the clean face by the evaporation of their solutions, into crystals whose edges are parallel to those of the large crystal. Barker and Beilby describe this phenomenon. The orienting power is lost or much diminished on exposure to the air for any length of time, probably because a layer of contamination forms." * [11]

From what has been said, it is evident that most surfaces involved in commercial or in laboratory work on cohesion or adhesion are not to be considered as simple, ideal, and invariable. They are generally composed of variable mixtures of substances which may themselves be quite complex, intermixed with impurities, and arranged in structures which may vary greatly within a narrow area. The past history of each surface and its present condition are always important. Wood is a striking example. Attention is drawn to the remarks on *surface specificity* in Vol II of this series, page 12. *It is a dominating factor in adsorption and catalysis, as well as in adhesion and cohesion.*

T. W. Richards,[12] in considering internal pressures, drew attention to the following statement in the third edition of Sir Isaac Newton's "Opticks."

"The parts of all homogeneal hard Bodies which fully touch each other, stick together very strongly . . . I . . . infer from their Cohesion, that their particles attract one another by some force, which in immediate contact is exceeding strong, at small distances performs the chymical Operations above mention'd, and reaches not far from the particles with any sensible effect. . . . There are, therefore, Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out."

To a considerable extent modern physical and chemical research have answered the question posed by Newton, and have shown that the attraction existing between *any* two material aggregates is due to the *residual* electrostatic forces outwardly directed from their surfaces in apposition. Thus with atoms, attraction depends mainly on the outer electron ring; with molecules, on the "secondary valences" or unsatisfied "fields of force," and with larger groups, on the summation of the residual electronic forces in sub-units in their surfaces. Since this question has been discussed at some length in the first papers in Volume I and Volume II of this series, it will be merely indicated here. *But its importance is vital.*

Newton speaks of "homogeneal hard Bodies"; and we commonly speak of substances or surfaces as "homogeneous." A moment's reflection will show, however, that the only physical units which are not *demonstrably*

* Quoted from Adam, "Physics and Chemistry of Surfaces," New York, Oxford University Press, 1930, p. 171.

heterogeneous, are electrons and protons, and even about these some scientists have their doubts. The inhomogeneity of molecules crops out in crystals, where they cling together much more strongly along certain surfaces than in others, leading to preferential lines of cleavage. This is strikingly shown in mica, which splits readily along one crystal plane, but which is quite tough lengthwise of the lamellae. Analogous phenomena are shown in many fibers, and in more complicated structures like wood. Perhaps the most "homogeneous" type of massive substance obtainable would be represented by a single crystal of rock salt, in which each atom is arranged in a regular cubic space lattice. Yet the experiments of Joffé [13] indicate that even apparently perfect crystals must have minute cracks and imperfections which reduce measurable cohesion below what it should be, and determine the line of premature fracture. The strength of rock salt calculated on the basis of electrical theory [14] is about 200 kg. per sq. mm. By cooling spheres of rock salt in liquid air and then immersing them in molten lead, Joffé [15] demonstrated in the mineral a strength in excess of 70 kg. per sq. mm., whereas on ordinary tests it shows only about 0.45 kg. per sq. mm.

The subjoined table and note, kindly prepared for us by Dr. Robert F. Mehl, shows that the full tensile strength of metals is not yet plumbed.*

DISRUPTIVE NEGATIVE PRESSURES [1] AND CRITICAL DISRUPTIVE VOLUMES [2] IN METALS WITH OTHER RELATED DATA, AT 30° C.

	Critical Disruptive Volume	Disruptive Negative Pressure kg./mm.^{2}	Disruptive Negative Pressure lbs./in.^{2}	Ultimate Tensile Strength,[3] Corrected kg./mm.^{2}	Ultimate Tensile Strength,[3] Corrected lbs./in.^{2}
Lead	1.27	340	322,000	2.1	3,000
Aluminum	1.32	734	694,000	120.0	170,000
Silver	1.29	896	848,000	32.4	46,000
Gold	1.24	1,262	1,195,000	(26.0)	(37,000)
Copper	1.33	1,399	1,325,000	133.5	190,000
Palladium	1.29	1,705	1,614,000	(38.0)	(54,000)
Tantalum	1.30	1,900	1,801,000	(93.0)	(132,000)
Platinum	1.26	2,210	2,090,000	(37.3)	(53,000)
Nickel	1.33	1,890	1,792,000	(126.0)	180,000
Cobalt	1.33	1,870	1,772,000	85.0	121,000
Iron	1.305	1,884	1,781,000	120.0	170,000
Tungsten	1.35	3,570	3,379,000	1190.0	1,700,000

Griffith [16] prepared fibers and rods of glass and of vitreous silica by drawing them slowly after heating to a high temperature, and found that they

* Taken from "Absolute Cohesion in Metals—Disruptive Negative Pressures and Critical Disruptive Volumes," Robert F. Mehl, *J. Am. Chem. Soc.*, **52**, 534 (1930).

[1] The Disruptive Negative Pressure is that negative pressure, corresponding to a three-dimensional loading, at which the metal lattice will no longer cohere.

[2] The Critical Disruptive Volume is the volume at which, upon increasing negative pressure, the metal lattice will no longer cohere but will disrupt.

[3] The values for Ultimate Tensile Strength found in the tables refer to the load supported by the metal test piece at fracture referred to the original cross-section of the test piece. Because of the reduction in cross-section which a metal suffers during elongation, including both that due to simple stretching and that due to constriction ("necking down") which takes place just prior to fracture, the actual load born is much greater. Accordingly, the values for the ultimate tensile strength as found in the tables is corrected by the percentage reduction in area to a "true ultimate tensile strength." The numbers in parentheses in the last two columns are uncorrected for reduction in area, no data being available.

Note on Significance of this Table. The Disruptive Negative Pressures refer to a three-dimensional loading, whereas the usual tensile loading appears to be one-dimensional, i.e., exerted in one direction, and supported by a plane perpendicular to the direction of loading. There is reason to believe, however, that during the "necking" process the stress distribution approximates a three-dimensional loading (see original paper). The result of a consideration of the various factors involved leads to the conclusion that the absolute cohesion in metals should permit values for ultimate tensile strength, slightly inferior but not far from those listed in the second and third numerical columns, and definitely of the same order of magnitude.

showed very large increases in tensile strength and in elasticity. Thus a glass which ordinarily showed a tensile strength of 17.5 kg. per sq. mm., after treatment rose to 222 kg. per sq. mm., the strength increasing as the fibers grew smaller. Extrapolation to molecular diameters indicated a limiting strength of 715 kg. per sq. mm. The instability of these brittle forms was evidenced by the fact that on scratching they reverted to the ordinary weak state. Drawn silica, though capable of being bent to a small radius, finally fractured like a Prince Rupert's drop, even the thick ends of the original rod being shattered by the elastic tremor, which somewhat recalls an explosive wave.

Griffith attributes the differences between observed and calculated strengths in brittle substances, to the existence in ordinary substances of large numbers of minute cracks, which, when tension is applied, cause excessive internal localization of stress.* This is no doubt true, for the formation of large numbers of crystal nuclei and their simultaneous growth would naturally tend to leave imperfections, if not actual voids, at the interfaces between the variously oriented space lattices. But another factor must be considered. If the cooling is quick enough, the crystals tend to be of colloidal dimensions, so that few, if any, voids are formed. This is, of course, a metastable state, upset by scratching, or, as Griffith found, by merely ageing; whereupon the ordinary "weak" state was reached. The shattering "wave" observed when the quartz filament "exploded," may be understood as a sudden rush, unbalanced on one side, of exceedingly tiny crystals towards the lower potential condition of larger crystals, albeit that this latter condition when established would result in weakening voids. Furthermore, the formation of larger crystals is, in itself, a move towards weakness, because molecular or atomic attractions are weaker along some crystal surfaces than along others, and lines of preferential cleavage would result.

A somewhat similar phenomenon is found in sulfur. When heated to its second zone of fluidity (over about 200° C.) and then suddenly chilled, sulfur yields a tough transparent flexible mass, capable of being stretched like rubber. Crystal growth soon sets in, accompanied by molecular aggregation, and the mass reverts to ordinary brittle sulfur.†

A. Smekal[17] points out that the properties of solids can be arranged into two general groups: (1) Structure Insensitive Properties, which show the same order of magnitude whether we deal with single crystals or with polycrystalline aggregates, e.g., density, energy content, thermal coefficient of expansion, X-ray lattice structure, etc.; (2) Structure Sensitive Properties, which change materially on plastic deformation, changing grain size, or the presence of traces of impurities, e.g., elastic limit, breaking strength, thermal and electrical conductivity, etc. F. Zwicky,[18] in following out this line of thought, advances the view that ideal crystals, though dynamically stable, are thermodynamically unstable. "The thermodynamically stable forms are not completely characterized by the space lattice as it is deduced from the X-ray structure analysis. On top of this primary structure, there is superimposed a secondary structure, which shows a perfect regularity also. In general it has to be interpreted as a slight periodic variation in density. The elementary spacing of this secondary structure will for most of the crystals be found in the region between 100 and 10,000 Å." It should be noted that this includes colloidal dimensions. Zwicky believes the opening of cracks

* The trick of tearing a pack of cards seems to lie in so manipulating them that only a few cards are being initially torn at any instant.

† *See also* paper by P. P. von Weimarn in this volume.

to be related to this secondary structure, which gives preferential lines of slip. It is now commonly agreed, upon the basis of X-ray evidence, that crystal surfaces are full of exceedingly fine cracks caused by the unbalanced forces on surface molecules as compared with those in the body of the crystal.

The question is here raised (J. A.) as to whether *atomic or molecular orientation within a crystal* may not account for planes of preferential cleavage, which also means that there are planes of higher strength. The "weak" planes would perhaps correspond to lines or planes *between* what the X-ray spectroscopist would term "unit cells," the strong ones being lines passing *through* such cells. This can be the case only when the "cell" has a real physical *raison d'être,* rather than being a purely statistical entity in which consecutive "cells" often share the same atoms, so that "planes of preferential cleavage" would pass through such atoms.

An interesting aspect of adhesion comes into evidence when local overheating causes carbonaceous materials to "burn" to the bottom of stills or flasks in the laboratory, or to the bottom of cook-pots in the kitchen. Very slightly scorched material may be removed with comparative ease; more deeply brown material is harder to remove, but may yield, if dried, to solvents like kerosene or to mild abrasives and soap. Highly carbonized material generally adheres so tightly, that scratching with a sharp edge or with hard abrasives will usually leave some adhering carbon.

It seems as if the nascent bonds appearing as the more or less profound chemical changes occur, tend to be satisfied by whatever is nearest; and this may be adjacent material, or else the container bottom. As the heating continues, larger and larger amounts of progressively simpler compounds are formed, with fresh surfaces, at the container bottom, making not only a *quantitative* difference in the material on the "burned on" area, but also a *qualitative* difference. The simpler compounds appear to have the more powerful nascent valences or uncontaminated surfaces. An analogous phenomenon appears in the cylinders of automobiles, where deposits of "carbon" of a highly adherent nature are a continual source of trouble. Here the high heat results in very profound decomposition of the hydrocarbons, and large amounts of newly formed "adherent" carbon are, no doubt, formed.

It is here opportune to quote some remarks of Thomas Graham: [17]

"A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid silica sol, and when it advances leads to pectization. In the jelly [of silicic acid] itself, the specific attraction in question, or *synaeresis,* still proceeds, causing separation of water, with the division into a clot and serum; and ending in the production of a hard stony mass, of vitreous structure, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense synaeresis of isinglass dried in a glass dish over sulphuric acid *in vacuo* enables the contracting gelatin to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatin, when dried in the manner described upon plates of calc spar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal synaeresis.

"Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but more greatly developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions."

In concluding these general remarks, it must be pointed out that *time* is an important factor in the making of tensile strength tests. Stress slowly

applied often brings out the *tearing* strength, a break occurring at some imperfection and the tear following along this. The imperfection is often a surface crack, as in metal parts lettered or stamped with a die,* or with glass scored by a diamond or a file. Quickly applied stress, assuming that it is not applied in lop-sided fashion, tends to bring many, most or all of the cohering areas into play simultaneously, with a result that greater tensile strength is recorded. A somewhat analogous experiment may be made with a leather sucker disc, such as boys often play with. This consists of a disc of wet leather with a string through its center, held by a knot on the under side of the disc. If this disc is closely pressed to a flat stone, atmospheric pressure and adhesion hold it so tightly there, that the stone may be lifted, if not too heavy. A slight imperfection in uniformity of adhesion of the disc may break the "vacuum" and allow the disc to "peel off"; and the stone falls if the lifting force is *slowly* applied. But a *sudden jerk* may lift the stone, even if an imperfection be present; for it takes a certain *time* for the leather disc to tear loose, especially if the imperfection in its application to the stone is but slight.

Adhesion and Adhesives.

The adhesive industry is, in a modest way, a key industry. There is hardly an article or material connected with our daily life which does not call for the use of adhesives in its production or distribution. Adhesives are used to make such diverse things as cradles and coffins; pianos, paper boxes and pocket-books; furniture and fabrics; books, matches and airplanes. Packages of all kinds are labeled with adhesives and cartons are closed by them. Adhesives seal untold millions of envelopes and affix postage and revenue stamps. In abrasive papers, cloth, belts and wheels, the sand, garnet, emery, carborundum or other cutting powder is held fast by adhesives.

The outbreak of the great war brought a speedy realization of the importance of adhesives. Our own National Research Council had a special Committee on Glue and other Colloids; and in England, when the Department of Scientific and Industrial Research took over, from the Conjoint Board of Scientific Societies, the investigations into adhesives, there was formed the Adhesives Research Committee, which has issued Reports,† the first in 1922, the second in 1926, and a third and final one is under preparation. The second contains results of extensive investigations of J. W. McBain and D. G. Hopkins ‡ [20] on "Adhesives and Adhesive Action," which showed that adhesive joints may arise from two sources. One is mechanical embedding of the film of adhesive in the pores and asperities of the surfaces to be joined; in the extreme case this yields a purely *mechanical joint*. The other is the only possibility in truly polished surfaces, such as a crystal face; namely, a *specific joint* due to specific molecular attraction between surfaces and adhesive. Where both these factors occur they strongly reinforce each other.

From their extensive experimental evidence, the following further conclusions were drawn:

Accumulated evidence tends to show that any fluid which wets a particular surface and which is then converted into a tenacious mass by cooling, evaporation, oxidation, etc., must be regarded as an adhesive for that surface.

* It is good practice to polish metal parts carefully, for this not only adds to their appearance and resistance to corrosion, but also tends to prevent failure in service.
† Obtainable from His Majesty's Stationery Office, London.
‡ A preliminary account of their work appeared in *J. Phys. Chem.*, 29, 188 (1925).

With the same adhesive between the surfaces of various materials there is some evidence of the existence of a parallelism between the strength of the joints and the mechanical properties (tensile strength, compressibility, etc.) of the materials.

Tests of the strength of thin films of adhesive, which yield highly accurate results, reveal not only that the tensile strength of the adhesive is often enormously greater than joints made with various types of test-pieces, but that large changes can be made in the strength of the adhesives before they appear in results with the test-joints. It is suggested that these direct tests of film strength are more significant and unambiguous than any other single test of a glue.

This last conclusion depends on a method of determining the strength of thin films of unattached adhesives made by drying their solutions on a surface to which they will not adhere, e.g., very lightly greased ferrotype plates. These and further experiments are also described in *J. Phys. Chem.* **30,** 114-125 (1926); *Ind. Eng. Chem.* **19,** 1005 (1927); and *J. Soc. Chem. Ind.* **46,** 321T (1927).

The table on opposite page summarizes some of the *quantitative work:*

For the proper understanding of the Table, the following statement is reproduced:

Qualitative Work

"The investigation was commenced by a qualitative study of a variety of glued or cemented joints, because there appeared to be no satisfactory method available for testing the degree of adhesion with such surfaces as glass, calcite, charcoal, etc. Qualitative data, as varied as possible, were required in order to discover and explore different possibilities and to formulate hypotheses of adhesive action. The joint were classified as 'very strong' or '+++,' 'moderate' or '++,' 'weak' or '+,' and 'very weak' or '0.' An additional sign was used to show that the adhesive film was still moist when the joint was broken, viz., a bracket round the equivalent mark, thus (0).

"The following points need to be borne in mind when considering the results:

(1) With certain few exceptions the time allowed for the drying of the adhesive was 24 hours, a period grossly insufficient for the majority of adhesives under the particular experimental conditions. Subsequent tests have shown that the time required is in many instances as much as 14 days or even more.

(2) The surfaces employed were only roughly plane so that it is more than likely that in places the thin adhesive film did not completely bridge the gap between the surfaces.

(3) The cemented areas differed considerably from material to material. In the case of copper the area was about 2 sq. in., whereas it was only about ¼ sq. in. with fused silica. In hand-testing, it is not possible to make even an approximate allowance for such differences.

"However, the results undoubtedly convey some idea of the strength of a joint made under ordinary practical conditions.

"The weakness of many joints was found to be due to the inability of the adhesive film to dry between two non-porous surfaces within a reasonably short period of time when the distance between them was small.

"It is possible, however, to alter the conditions of the experiment so that the film can dry quickly by the device of adopting a joint of the type.

Material : Adhesive : Wood.

"Usually the adhesive : wood linkage will not yield first, and the strength of this 'mixed' joint generally depends on the strength of the bond between material and adhesive. With most adhesives two sets of experiments have been carried out, one with the simple type of joint (material : adhesive : material) and the other with the 'mixed' type (material : adhesive : wood).

"No very carefully prepared test-pieces were used. The surfaces were, however, cleaned thoroughly (oxide films removed as far as possible from metals, washing with suitable solvents, etc.) before applying the adhesive. For wooden joints, planed deal was

TABLE 1.—*Qualitative Classification of Various Adhesives with Various Materials.*

	Gelatin X	Gum Arabic	Starch	Adhesive A	Adhesive B	Silicate of Soda	Adhesive C	Nitro-cotton	Adhesive D	Casein and Borax	Glycerin Cement	Canada Balsam	Shellac Wax Free Molten	Shellac Wax Free Alcoholic	Shellac Ord. Alcoholic
Wood : wood	+++	+++	+++	+	+++	+++	+++	+	+++	+++	(0)	(0)	+++	+++	+++
Porcelain : porcelain	+++	++	+0*	+	+++	++	++	0	+++	+++	(0)	++	+++	+++	—
Porcelain : wood	+++	++	+	+	—	—	—	—	—	—	—	—	—	—	+++
Pumice : pumice	—	—	—	(0)	++	++	(+)	—	—	—	(+)	—	—	—	—
Pumice : wood	—	—	—	—	+++	+++	+++	—	—	—	—	—	—	—	—
Charcoal : charcoal†	+++	+++	++	0	+++	++	(0)	0	+++	+++	(0)	(+)	+++	0	—
Charcoal : wood	+++	—	—	—	—	—	—	—	—	—	—	—	—	—	—
F. silica : F. silica	—	+	(0)	(0)	(0)	(+)	(+)	0	+++	—	(0)	(0)	+++	(+)	—
F. silica : wood	+++	0	0	0	+++	+++	+++	—	+++	+++	(0)	—	—	—	+++
Glass : glass	—	—	—	(0)	(0)	(+)	++	0	+++	—	(0)	(+)	+++	(+)	—
Glass : wood	+++	—	—	0	+++	+++	+++	—	—	+++	(0)	—	—	—	+++
Mica : mica	—	(0)	(0)	(0)	(0)	(0)	—	—	—	—	—	(0)	—	(0)	—
Mica : wood	—	0‡	0‡	0‡	(‡)	(‡)	—	—	—	—	—	—	—	—	—
Ebonite : ebonite	—	(0)	(0)	(0)	(0)	(0)	(0)	0	0	—	(0)	(+)	+	(+)	—
Ebonite : wood	0	0	0	0	0	0	0	—	—	0	(0)	—	—	—	++
Calcite : calcite	—	(0)	(0)	(0)	(0)	+++	(0)	0	+	—	(0)	(0)	+++	(0)	—
Calcite : wood	++	0	0	0	0	+++	0	—	—	+	(0)	—	—	—	+++
Rubber : rubber	—	(0)	(0)	(0)	(+)	0	(+)	+	0	—	(0)	(0)	0	++	—
Rubber : wood	++	+	0	—	+	0	++	—	—	+++	(0)	—	—	—	—
Lead : lead	—	(0)	(0)	(0)	(0)	(0)	—	—	(+)	—	(0)	(0)	0	(0)	—
Lead : wood	0	0	0	0	0	0	+	0	—	0	—	—	—	—	0
Tin : tin	(0)	—	—	—	—	—	(0)	—	(+)	—	(0)	—	+	—	—
Tin : wood	0	—	—	—	0	+	+	0	+++	++	—	—	—	—	+++
Al : Al	—	(0)	(0)	(0)	(0)	(0)	—	—	—	—	(0)	(0)	0	(0)	—
Al : wood	—	0	0	0	0	0	0	—	—	—	—	—	—	—	—
Copper : copper	(0)	—	—	—	—	—	—	—	(+)	—	(0)	—	0	—	—
Copper : wood	0	0	—	—	0	0	0	0	+	+	—	—	—	—	0
Steel : steel	(0)	(0)	—	—	—	—	—	—	(+)	—	(0)	—	0	—	—
Steel : wood	0	+	—	—	+	+	0	0	+	+	—	—	—	—	0
Nickel : nickel	—	—	—	—	—	—	—	—	—	—	(0)	—	—	—	—
Nickel : wood	—	—	—	—	—	—	—	—	—	++	—	—	—	—	+++

* The starch film on porcelain was excesively thin and certainly incomplete.
† Gas carbon with casein borax cement gave only a weak joint
‡ Difficult to decide whether joint was broken or whether mica split across a cleavage plane.

employed. The porcelain was broken from unglazed plates. The charcoal was generally blocks of wood charcoal but gas carbon was used in one or two instances. Optically polished plates of fused silica were used. The remaining designations are as follows:—

Glass. Plates of ordinary plate glass.
Ebonite. Ordinary slabs with polished faces.
Calcite. Medium sized crystals.
Rubber. Rubber stoppers.
Metals. Small sheets of the commercial variety.

The following adhesives were made use of:

Coignet's Gold Label Gelatin X, with the maximum quantity of imbibed water, heated on a water bath.

Gum Arabic.—40 per cent aqueous sol.

Starch.—About 5 grams of powdered starch were rubbed into a fairly thin paste with cold water. This paste was then slowly added with constant stirring to about 50 c.c. of boiling water and allowed to simmer for a few minutes. The gelatinous mass formed on cooling was used as the adhesive.

Adhesive A. (Starch Base)
Adhesive B. (Animal Glue)
Adhesive C. (Fish Glue)
Adhesive D. (Nitro-cellulose base)
} Proprietary preparations applied according to directions.

Silicate of Soda. Proprietary Brand. A molar ratio ($SiO_2 : Na_2O$) $= 3{\cdot}3$ was used for all materials except tin, copper and steel when a molar ratio of 2·0 was used.

Nitro-cellulose.—2 grams of dry nitro-cotton treated with 25 c.c. of alcohol-ether mixture (5 vols. alcohol to 2 vols. ether-mixture with maximum solvent effect).

Casein and Borax Cement.—Casein was added to a cold saturated solution of borax with constant stirring until a viscous sol was obtained.

Glycerin Cement.—50 grams of litharge were triturated with 6 c.c. of a solution consisting of 5 vols. of glycerin and 2 vols. of water.

Canada Balsam.—About 5 c.c. of benzene were added to 2 grams of Canada balsam and the mixture heated on a water bath until a viscous sol was obtained.

Shellac.—The wax-free shellac used in two sets of experiments (molten shellac in one and an alcoholic solution in the other) was kindly supplied by Sir Herbert Jackson. In the third set of tests with alcoholic shellac the ordinary commercial variety was employed. In the case of the molten shellac the materials were heated until the shellac melted on the surface. The alcoholic shellac was prepared by warming the shellac with methylated spirits until a somewhat viscous sol was obtained.

"In most cases the joints were set up under hand pressure. Pressure applied by means of a vice was necessary with the metal and certain other joints in order to bring the opposing surfaces within sufficiently close range of each other. It is advisable to consider first the special experiments which were carried out with silver and gelatin as they greatly enhance the significance of the results to follow.

The Effect of Surface Porosity on the Strength of Joints

"The following experiments were performed in order to ascertain the effect of surface porosity on the strength of joints. Three forms of silver plates were employed with gelatin; namely, silver plate with smooth surface, (S), silver plate on to which a piece of silver gauze was welded at several points, (S)g, and silver plate on to which two layers of silver ganze were spot welded (S)gg. A concentrated sol of gelatin X was used, the time of drying in all cases being 4 days.

TABLE 2.—*Experiments Demonstrating Existence of Mechanical Joints.*

Joint	Strength	Remarks
1. (S) : Gelatin : (S)	Very weak (0)	Film moist.
2. (S)g : Gelatin : (S)g	Very weak (0)	Film moist.
3. (S) : Gelatin : Wood	Very weak 0	—*
4. (S)g : Gelatin : Wood	Weak +	Joint stronger than 3.†
5. (S)gg : Gelatin : Wood	Moderate ++	Joint stronger than 3 or 4.†

* Film adhered wholly to the wood when the joint was broken.
† When these joints were broken, the film adhered partly to the silver gauze and partly to the wood.

"Similar results were obtained with gum arabic, and with molten shellac (no metal: wood joints required in the latter case).

"These experiments besides demonstrating the effect of certain porous bodies in drying the film of adhesive, conclusively prove that a strong joint may be made by purely mechanical embedding of the adhesive in the porous surface. This type of joint is in sharp contrast to those between polished surfaces which must depend upon specific interaction between surface and adhesive. It is thus possible to state that strong joints may be made without adhesiveness and it will be shown that glued wooden joints appear to belong essentially, although perhaps not exclusively, to this specific mechanical class."

Quantitative tests were made with a number of adhesives, as described below:

"It is necessary to record a few notes about some of the adhesives and the method of applying them.

Shellac.—The wax-free shellac used in these experiments was kindly supplied by Sir Herbert Jackson and consisted of pure shellac freed from wax by the following process. The shellac is dissolved in alcohol and the solution is filtered through a layer of sand on a filter-paper. The alcohol is distilled off from a water bath until the solution attains the consistency of treacle. This viscous solution is poured out on a glass plate and the rest of the alcohol evaporated at a temperature of from 40° to 50° C. The shellac so obtained appears to be free from wax but it would contain fatty acid if such is present in the shellac in the free state. It would also contain a little residual alcohol. It is quite pliable at room temperature.

The metal test-pieces were placed on a metal plate which was heated until the temperature of the test-pieces was sufficiently high to cause the shellac to melt on the surfaces and further heat was applied to render the cement fluid. The surfaces were then brought together with a sliding motion and pressure was exerted in order to remove superfluous cement.

Alcoholic shellac was prepared from the ordinary and wax-free variety by heating with 98 per cent alcohol until a moderately viscous solution was obtained. Opposing surfaces were coated with this adhesive and brought together in the usual way. In no single instance was the shellac solution dry after a period of six weeks. The purely nominal strength of practically all the joints was in the region of 100 lb. per sq. in.

De Khotinsky Adhesives E. are well known American preparations with a shellac basis and a faint odour of creosote and are supplied in three grades. These cements are applied in exactly the same way as molten shellac.

Shellac-creosote Cements.—The following cements were supplied by Sir Herbert Jackson. The numbers indicate parts by weight.

TABLE 3.—*Composition of Shellac-Creosote Cements.*

Composition	Distinguishing Numbers of Cement					
	I	II	III	IV	V	VI
Shellac, brown	50	—	—	—	—	—
Shellac, orange	—	50	50	50	50	50
Creosote	5	5	5	5	5	5
Ammonia	—	0.5	0.5	—	—	1
Turpentine	—	2	—	—	—	—
Terpineol	—	—	—	—	2	2
Formanilide	—	—	—	5	—	—

Beechwood creosote was used in compounding each cement. In cements V and VI terpineol was employed instead of turpentine as it is a solvent for shellac whereas the turpentine used in II is not. The adhesive was applied in exactly the same way as molten shellac.

Adhesive F.—This is a wax of a resinous nature and melts at a lower temperature than shellac. Method of application as for shellac.

Adhesive G.—The proprietary marine glue is a combination of shellac and india-rubber in proportions which vary according to the purposes for which the cement is

required. The degree of softness is also regulated by the proportion of coal tar naphtha used for dissolving the ingredients. When used it is heated to its melting point and applied to the warm metal surfaces.

Nitrocellulose Adhesive D.—is a colourless, viscous fluid smelling strongly of amyl acetate. A very thin coating of the cement is applied to each of the clean dry surfaces to be joined and allowed to dry naturally in the air. This preliminary treatment is essential for a good joint. A second coating of the cement is then applied to each surface and while still wet the two surfaces are brought together and kept in close contact until the cement hardens.

With certain metals, viz.: copper, brass, mild steel, cast iron and lead there were signs of slight chemical action.

Gum Arabic.—10 grams of the gum are dissolved in 20 c.c. of distilled water heated to 60° C. With the exception of the wood joints the method of double coating was employed in all cases.

Canada Balsam.—The adhesive solution was prepared by warming a mixture of the balsam and benzene, 5 grains to 5 c.c., on a water bath. The method of double coating was employed. Even after a month had elapsed the adhesive was still moist. The joints were heated at 100° C. for a further two days before testing.

Coignet's Gold Label Gelatin X.—The solution was prepared by soaking 5 grams of the gelatin in 20 c.c. of water overnight, subsequently heating on a steam bath. In the tests carried out with all materials other than wood two coatings of the adhesive were applied to each surface except where otherwise indicated.

In setting up the wood joints (Table 15) the gelatin solution was prepared by heating gelatin holding the maximum quantity of imbibed water on a steam bath.

Cannon's Propeller Glue H.—A high grade animal glue. The solution was prepared, except where otherwise stated, by heating 20 grams of the glue soaked in 50 c.c. distilled water overnight. With the exception of the wood joints the procedure of doubly coating each of the surfaces was followed.

Fish Glue.—Was prepared on the large scale by Dr. Kernot from skins of cod and haddock. (*See* Appendix III.) Experiments were carried out with the fish glue itself and also with a modified fish glue which had been made to imitate a high grade gelatin (melting point of 10 per cent. sol = 31° C.) by adding bone gelatin to the original fish glue. In the wood tests the solutions were prepared by allowing the glues to stand in water overnight, decanting the superfluous water and heating at 60° C. On standing in water the ordinary fish glue showed a pronounced tendency to pass into a sludge. The modified fish glue retained its form.

In the experiments carried out with the metals a 25 per cent. aqueous solution was employed and the surfaces excepting those of wood were doubly coated.

Isinglass.—Solution prepared from 5 grams isinglass (refined) and 25 c.c. distilled water in precisely the same way as the gelatin solution.

Adhesive K.—A proprietary fish-glue preparation. The procedure of doubly coating the surfaces was again adopted except for wood joints.

Silicates of Soda.—Through the courtesy of the manufacturers a complete series of solutions of silicate of soda, including various 'Commercial' brands and experimental samples, was placed at our disposal. According to information supplied by the manufacturers it is important not to disturb the joints once they have been set up as any subsequent rupture of the silicate bond is supposed to have a very deleterious effect on the strength of the joints. This point has not yet been tested. The surfaces of many metals reacted somewhat with certain grades.

In a few tests a French preparation containing a silicate but otherwise of unknown composition was employed.

Casein and Silicate Cement.—Pure casein (3 grams) added to 20 c.c. Grade 3 Silicate of Soda in small portions with vigorous stirring.

Casein and Borax Cement.—Pure casein (5 grams) was added to 20 c.c. of a cold saturated solution of borax, as above.

Rubber Solution.—Double coating applied to all surfaces.

Starch.—5 grams starch powder and 5 c.c. of cold water were rubbed together in a mortar. The mixture was added to about 50 c.c. of boiling water and the resulting mucilage kept at boiling point for a minute or so. It was applied while still warm.

Adhesive L.—The manufacturers state that this preparation is a starch ester, possessing all the usual starch characteristics except that the paste prepared from it does not set on cooling.

Adhesive M.—A metallic jointing compound for internal combustion or steam engines, containing powdered aluminium. It was thinly spread on the opposing sur-

TABLE 5.—*Tension and Shear Tests—Adhesive between Metal Surfaces.*
(Representative values are given in lb. per sq. in.)

Adhesive	Test	Time of Drying or Setting (days)	Nickel	Mild Steel	Cast Iron	Copper	Brass	Alu-minium	Tin	Lead
Molten Shellac (Purified) ...	Tension	1-5	3,500	3,200	3,000	3,300	2,500	2,800	1,100	600
	Shear	1-3	—	3,400	3,000	3,300	3,300	2,200	—	—
Adhesive E ("Hard").......	Tension	1-2	4,200	4,800	4,400	4,000	2,900	2,300	1,500	500
	Shear	1-3	—	4,200	4,100	4,100	3,800	3,100	1,100	600
Adhesive E ("Medium")....	Tension	1	-	—	—	4,400	—	2,400	—	—
	Shear	1	—	3,700	3,200	3,400	3,500	2,100	—	—
Adhesive E ("Soft")........	Tension	6	4,400	4,600	3,200	4,000	3,900	2,800	—	—
	Shear	6	4,000	4,400	3,700	4,700	3,500	(2,600)	—	—
Adhesive F	Tension	1-2	1,200	1,000	1,400	1,000	1,100	1,000	800	500
	Shear	1	500	—	—	500	600	600	600	600
Adhesive G	Tension	4-5	1,100	1,700	900	1,000	1,500	1,400	800	—
	Shear	4-5	600	1,200	800	600	500	900	900	—
Adhesive D	Tension	14-21	1,600	1,600 *§	1,400 ‡	2,000 †‡	1,500	1,700	1,000	500
	Shear	21	—	700	800	500	500	800	600	400
Gum Arabic	Tension	77	1,200	900	1,100	1,600	1,600	700	800	—
	Shear	77	1,200	1,300	1 000	1,300	600	1,500	800	—
Canada Balsam	Tension	27	—	900	—	—	—	400	—	—
	Shear	27	300	—	400	—	400	400	—	—
Gelatin X	Tension	17	900	1,000	1,100	1,200	700	(300)	800	800
	Shear	20	—	1,000	700	800	1,100	—	500	—
Adhesive H	Tension	30	(400)	(1,300)	1,000	1,200	—	1,900	900	800
	Shear	30	(600)	(1,500)	1,300	1,300	—	1,400	700	—
Fish Glue	Tension	16	1,200	800	1,200	1,400	700	1,000	—	—
	Shear	16	500	1,400	1,200	1,100	1,400	(200)	—	—
Adhesive K	Tension	18	—	—	—	300	—	400	400	—
	Shear	18	—	500	400	500	300	300	—	—
Silicate of Soda, Grade 1....	Tension	17	200	200	200	300	200	200	200	—
	Shear	17	200	200	200	200	200	200	—	—
Silicate of Soda, Grade 2....	Tension	17	500	500	500	600	500	400	500	—
	Shear	17	400	500	400	500	400	400	400	—
Silicate of Soda, Grade 3....	Tension	26	1,000	1,200	1,000	1,100	1,400	900	900	700
	Shear	26	600	800	600	1,100	900	500	400	—
Silicate of Soda, Grade 4 ...	Tension	26	1,300	1,300	1,100	1,400	1,500	700	1,000	—
	Shear	26	800	900	800	1,000	1,200	700	700	—
Rubber Solution	Tension	16	—	—	300	—	—	—	—	—

* If the surface of the steel is first oxidised in the blow pipe flame this value becomes 900, showing distinct weakening.

† Amalgamation followed by complete removal of excess of mercury by rubbing the surfaces with cotton wool and allowing several days for penetration before making the joints reduces this value to 400. In two cases the adhesive film separated from both surfaces intact and its thickness was 0.003 in. and 0.0015 in. respectively.

‡ Roughing the surface of the test piece with No. 3 emery cloth leaves these representative values unchanged.

§ Roughing the test piece with a spiral groove (pitch 1/48 in.) in the lathe with a round nose tool of 1/32 in. radius reduces this value to 1,100.

faces of steel testpieces and the joints were heated to about 230° C. for 15 minutes and tested after 9 days.

Summary of Results.

"In order to economise space the representative values only are given in the following Tables 4 to 7. In most cases they are derived from at least four experiments and often from eight. As a general rule the differences between the maximum and representative values are comparatively small."

TABLE 4.—*Tension and Shear Tests—Shellac-Creosote Cements between Metal Surfaces.*

Representative values in lb. per sq. in.; period of setting 1–4 days.

Cement Number	Tension	Shear
I	4,400	3,400
II	4,900	4,800
III	4,000	4,600
IV	3,300	2,500
V	4,000	4,300
VI	4,400	3,400

TABLE 6.—*Tension Tests—Adhesives between Optically Plane Metal Surfaces.*

(Maximum values of the strengths of joints in lb. per sq. in.)

Adhesive	Metal	Maximum Strength of Joint	
		Optical Surface *	Ordinary Surface
Adhesive E ("Hard")†	Mild Steel	3,800	4,900
	Nickel	3,900	4,800
Shellac-creosote cement II	Mild Steel	5,600	5,000
	Nickel	6,400	—‡

* Prepared at the National Physical Laboratory.
† A new sample of this cement had to be used in the experiments with the optical surfaces. Difference in quality probably accounts for the observed differences.
‡ Not determined but probably about the same as for mild steel.

"Perhaps the most striking result is the remarkable strength of some of the joints set up with shellac cements between smooth metal surfaces. A few such joints have attained a strength of 2¼ tons per sq. in. in tension and shear whereas the best glued wood joints rarely exceed 1,200 lb. per sq. in. A few preliminary experiments have proved that film thickness is an important factor in adhesion phenomena. Crow,* in a systematic study of soft soldered joints has shown that by making the film of solder very thin the strength of the resulting joints may be as great as 11 tons per sq. in., the tensile strength of the solder being exceeded several fold. However, such joints were apparently not strengthened very appreciably when the thickness was diminished from 0.2 mm. to the thinnest attainable and the results are influenced by the alloying which occurred. That thin films are very much stronger than an adhesive *en masse* is established by Crow's result for soft solder and our much more striking instance of a wax free shellac. Joints made with this shellac, which is fairly soft and quite pliable, actually withstood a pull of nearly 4,000 lb. per sq. in. when a thin film was used between nickel surfaces. We have found that optically plane surfaces prepared at the National Physical Laboratory yield stronger joints than those which have not been prepared with such precision. An examination of the broken joint served to show how exceedingly thin was the film between those highly polished surfaces. The amount of adhesive attached to the metal was just sufficient to dim the lustre. Incidentally the results of the tests carried out with a shellac-creosote cement between optically plane surfaces of mild-steel and nickel

* *Trans. Soc. Chem. Ind.*, 43, 65 (1924).

TABLE 7.—*Shear Tests—Adhesive between Walnut Surfaces (R.A.E. Joints).*
(Representative values in lb. per sq. in.)

Adhesive	Period of Drying (days)	Strength of Joint lb. per sq. in.
Fish glue	7	1,400
Adhesive H	5	1,300
Gelatin X	6	1,200*
Adhesive K	7	1,200
Gelatin, highly purified	6	1,100
Fish glue with added bone gelatin	7	700
Casein and borax cement	6	600
Gum arabic	6	400
Adhesive B	12	400
French adhesive (silicate preparation)	8	300
Casein and silicate cement	8	300
Adhesive D	30†	300
Starch	9	300
Adhesive L	7	100
Silicate of soda—		
Grade (5)	28	300
Grade (1)	28	400
Grade (2)	28	500
Grade (3)	28	700
Grade (4)	28	400
Experimental I	15	0
Experimental II	15	0

* This value is reduced to about one-third if the joint be heated at 100° C. for four days when securely clamped to prevent distortion.
† It is a matter of some difficulty to join surfaces of large area with this cement as it sets rapidly on exposure to the atmosphere. On the other hand it dries very slowly between hard wood surfaces.

prove beyond doubt that surface roughness plays but a negligible part in determining the strength of a 'specific' joint for here we have the smoothest possible surfaces yielding stronger joints than those prepared in the ordinary way and which are therefore comparatively very rough. Other experiments indicate quite clearly that if metal surfaces be rather deeply furrowed in the process of roughing then the joints are decidedly weaker than those obtained with smooth surfaces, the lower results presumably being attributable to (I) an increase in the average thickness of the adhesive film (II) insufficient adhesive to bridge the gap completely between the surfaces, and (III) the increased difficulty of eliminating air bubbles. It should be added that the precautions taken in obtaining exceedingly thin films result in a more rigorous exclusion of air bubbles and consequently in a greater completeness of film.

"Reference may conveniently be made at this point to the opinion expressed by Crow that in soldered joints it is essential that diffusion (alloying) should take place. The whole weight of the evidence brought forward in the present inquiry runs contrary to this conception of adhesive action for there would appear to be no valid reason for assuming any fundamental difference between soldered and glued or cemented joints.

"When the joints between metal surfaces are set up with gelatin, Adhesive D, etc., merely by bringing together the surfaces with a single coating of adhesive, the results almost invariably fluctuate considerably. If, however, the first thin coating of adhesive is allowed to dry thoroughly before applying the second coating just previous to bringing the surfaces together the results are generally higher and more concordant than those obtained in the simpler mode of application of the adhesive. The probable explanation is that the method of 'double coating' gives rise to more complete adhesive films. Other observers have noted similar results with glued wood joints. It is probable that better results would be obtained with most adhesives if this procedure of double or even triple glueing were adopted.

"Shear tests carried out with a large number of adhesives between walnut surfaces demonstrate very plainly that gelatin preparations are far in advance of other adhesives. It is very interesting to note that highly purified ash free gelatin is little, if at all, inferior to a first grade commercial gelatin or glue. In these wood joints the adhesive is regarded as embedded in the pores and surface irregularities. It is somewhat signifi-

cant, however, that their strength is only a small fraction of the tensile strength of the adhesive itself. Experiments to be described later show the tensile strength of a high grade commercial gelatin or glue to be about 13,000 lb. per sq. in. Of course, with glued walnut joints failure almost invariably takes place in the wood itself or in the layer where the glue film is weakened by the embedding in the wood. With less tenacious adhesives such as gum arabic, silicate of soda, etc., where the failure occurs in the adhesive the strengths of wood joints ought to run parallel with the tensile strengths of the adhesives. Later experiments indicate that a good glue has considerable 'reserve' strength, for a 'doctored' glue with a tensile strength of just over 7,000 lb. per sq. in. would appear to give walnut joints equally as strong as those set up with a glue with a tenacity of nearly 13,000 lb. per sq. in.

"The thinness of some of the adhesive films probably accounts for the weakness of certain joints. The results in Table 16 show the possibilities of a so-called weak adhesive like starch paste. When walnut surfaces were given one coating of starch paste or of a commercial vegetable glue it was almost impossible to detect the semblance of a film on the surface when the adhesive had dried. Walnut joints of the R.A.E. type set up between surfaces singly coated with starch paste were only one quarter as strong as those made with a high grade glue. Using double cover plate joints and surfaces trebly coated with starch paste the ratio of the strength of the joints with the two adhesives was 1 : 2. With the vegetable glue the joint strength increased quite appreciably when three coatings were used instead of two."

The strength of a joint made between smooth non-porous surfaces would seem to be dependent upon the nature of the material, even when there is no sign of chemical interaction. As yet the data are far from complete and not sufficiently free from disturbing factors to establish any general rule with certainty. The experimental difficulties are such as would make one extremely cautious in associating joint strength with any other property. The presence on imperceptible films of a metallic oxide or of grease might invalidate any result. The preparation of chemically clean surfaces is a matter of considerable difficulty. Variations in film thickness would certainly account for many observed differences in joint strength. When comparing the strengths of joints made with different materials, it is necessary to assume that all the surfaces are equally true and that no distortion of the surface takes place when the test is being made. These assumptions are not always justifiable; in the case of materials with low yield point, such as lead and tin, sufficient distortion probably occurs, with many adhesives, to affect results.

That many pure chemical compounds will function excellently as adhesives, is demonstrated by the work of J. W. McBain and W. B. Lee.[3] They divided the compounds used into three groups, according to the strength of the joints obtained in cementing together various metals; and these joints differed from one metal to another, for the same substance.

1. *Strong*, of the order of 1,000 lbs. per sq. inch.
   Rochelle salt, glucose, triphenylcarbinol, *p*-hydroxybenzaldehyde, benzophenone, benzil, T.N.T. (2:4:6 trinitrotoluene), salicin, cholesterol.
2. *Medium,* of the order of 700 lbs. per sq. inch.
   p,p-Diaminodiphenylmethane, thallium salicylaldehyde, benzophenone, coumarin, saligenin (first heated to resinification), biuret.
3. *Weak,* of the order of 500 lbs. per sq. inch, or less.
   Methyl-*d*-glucoside, thallium maleate, a saturated aliphatic hydrocarbon $C_{26}H_{54}$, phenanthrene, camphene, sodium palmitate (m.p. 316° C.), salol (joint innoculated to cause setting), saligenin heated only to its melting point.

There was no definite connection between melting point and joint strength, but most substances yielding strong joints contained –OH or –CO– groups. A direct parallelism exists between joint strength and the mechanical properties of the materials joined, the joint strength rising with tensile strength and elasticity, and falling with increase in atomic volume.

A good lubricant is a poor adhesive, and McBain and Lee suggest that this may be due to molecular orientation at the contact interface (metal), leaving the less active groups outwardly directed into the "adhesive." Where the valencies are so directed that a chain effect obtains, the material holding to itself as well as to the metal surfaces being joined, then the substance is an antilubricant or a good adhesive.

Pure liquids may also function as adhesives. In testing them, McBain and Lee used optically plane metal surfaces prepared by the National Physical Laboratory (Teddington, Eng.), and after moistening the metal faces with the liquid under test, wrung them together by a combined sliding and twisting motion, along lines suggested by Budgett,[21] to make a thin film. The following results were obtained:

Liquid	Breaking load in lbs. per sq. inch
Water	14.7 to 36
Ethyl acetoacetate	13.2 to 26 (grips blocks well in shear)
Oleic acid	up to 10.0
Ethyl oleate	5.2 to 15.2
Olive oil	up to 12
Triolein	7.2 to 10.1
Castor oil	7.2 to 9.1
Ethylene glycol	8.0 to 1.6
Benzene	up to 10.2
Iodobenzene	6.5 up to 20.0
Quinoline	up to 20.0
Linseed oil	11.8 to 18.5
Furfurol	7.9 to 12.0
Phenylacetylene	up to 14.0
Methylenemalonic ester	7.8 to 10.2
Ethyl acetate	9.5 to 15.4
Ethyl benzoate	up to 14.0
Ethyl phthalate	up to 21.0

In all cases, the thinner the film, the stronger the joint.

In a recent review [22] W. B. Lee points out that in 1875 Tyndall "wrung" together two Whitworth surfaced plates and then suspended them *in vacuo*, proving that their adherence was not due entirely to atmospheric pressure, as with the Magdeburg cups. He invoked partial molecular contact to explain the phenomenon. Just previously, Stefan [23] had shown that the attraction between two polished plates depended on their size, their distance apart, and the *nature of the fluid in which they were immersed*, being greater in liquids than in air. He differentiated between real and "apparent" adhesion, and pointed out that when tension is applied, dilation of the intersurface liquid sucks in more liquid; but this involves a time-factor.

Lee concludes that the *effective* range of molecular attraction may be hundreds of molecular diameters as held by all the older physicists and by Sir Wm. B. Hardy since 1928, or else that there is a chain effect in molecular orientation, which *simulates* a large direct range of attraction, as suggested by McBain and by Hardy in 1927.

If a trace of paraffin be smeared on a rod carefully ground to fit a hollow cylinder, the rod enters and continues on unless it be allowed to stand quiet for a few moments. In this case, the paraffin film apparently "goes solid," but may be "fluidified" by a sledge hammer blow accompanied by a twisting motion. It seems quite possible that molecular orientation is of such a nature that with polar substances chains or "fibers" are formed, even though they be short, with their ends fixed in the opposing surfaces. If these fibers tend to assume random orientation, we would have a strain which would tend

to bring the surfaces closer. In this connection, see the papers of P. P. von Weimarn in this volume.

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Some Practical Results of X-ray Researches on Colloids

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When Sir William Bragg wrote his chapter on "Colloids and X-rays" for Volume II of this work, actual experimental data were still comparatively scanty. In straightforward fashion he outlined clearly five fundamental points in respect to which knowledge of the colloids is to be desired—such knowledge as X-ray diffraction analysis may be expected to contribute: The internal structure of the colloidal particle; the nature of the exterior layers; the average size and distribution around the average; the general shape or form of the particles; and tendencies to orient. Speaking of cellulose, one of nature's great colloids concerning which some information had already been obtained, this great pioneer in X-ray science said, "The time will surely come when we shall know the place taken by each atom in the pattern."

As now in 1931, we survey the field, we marvel at the accuracy of this prophecy. We are amazed at the progress which has been made by bringing together in research the X-ray method and colloids with rapidly improving technic and with deepening knowledge of interpretation. In fulfillment of the prophecy concerning cellulose we find before us a table of the exact coordinates in space of every carbon and oxygen atom in cellulose and a complete structural model, including the size, shape, structure, binding and orientation of the colloidal micelle, which must be correct in its essential details because it depicts so perfectly all the observable properties of textile fibers. Rayon has been very greatly improved in its properties by an X-ray study of the effect on structure of every detail in the manufacturing process, from the raw material to the dyed fabric. The actual age of a growing cotton fiber can now be ascertained, and cotton classified as to quality by the X-ray pattern alone. Some of the most difficult problems concerning growth, structure, and technical uses of wood have been already successfully attacked, though researches have hardly begun. The structure, fundamental properties, colloidal particle size, and classification of natural silk and wool (both proteins), pectin, gelatin, collagen, body tissues, plastic films of cellulose acetate and nitrate used for photographic films or of cellophane, soap solutions, resins, linseed oil films (paint, patent leather) and many other substances classed as colloidal, besides the familiar sols of metals or salts, have been subjected to X-ray study with most interesting and promising results, in spite of the complexity of constitution in many instances. Before a summary of some of these developments is made, it is advisable to review briefly the fundamental principles of colloid classification and of X-ray diffraction by colloidal materials.

X-Ray Diffraction by Crystalline and Amorphous Substances.

It is, of course, now widely known that crystals act as three dimensional diffraction gratings for X-rays by virtue of the arrangement of the lattice units

(atoms, ions, molecules or groups of these) on sets of equidistant parallel planes. With a beam of monochromatic rays passing through a specimen, a pattern on a photographic plate is obtained, which is absolutely characteristic of the material—whether it is crystalline or amorphous, what are its crystallographic system and space group defining coördinates in space, and the interplanar spacings, whether it is a single crystal or an aggregate, whether the aggregate has random or preferred orientation of grains, whether it is a single pure substance or is a mixture of two or more individuals or a solid solution, how large the grains or particles are or how thick a film, and whether there is distortion or strain. It follows that an amorphous substance would merely scatter X-rays in all directions and produce a general fogging of the photographic plate without evidence of diffraction interference maxima, whereas any kind of arrangement of ultimate units, even though very imperfect, would produce a diffraction pattern characterized by interference maxima. Even a single diffuse broad diffraction ring indicates at least an elementary tendency towards organization. One of the most remarkable facts from X-ray science is the extreme rarity of the true amorphous state. Repeatedly it has been found that a specimen which by all ordinary methods of examination appears to be amorphous, produces unmistakable evidence of an organized ultimate structure under the searching scrutiny of radiation with wave-lengths only 1/10,000 as long as ordinary light, by means of which microscopic examination is made. Even liquids produce diffraction halos indicative of transient arrangement of molecules governed by distances of nearest approach in their thermal agitation, and designated by Stewart as "cybotaxis." And just now results on diffraction halos from gases have given evidence of the true structure of atoms in the sense of the distribution of diffuse wave like negative electricity according to Heisenberg and Compton, instead of sharply corpuscular electrons moving in orbits as depicted by the Bohr theory.

Diffraction by Colloids.

A single crystal subjected to analysis by the pinhole method produces a Laue diffraction pattern characterized by a symmetrical array of spots, lying on a series of ellipses. As the size decreases and more individuals lie in the path of the beam, this symmetrical pattern gives way to a random "peppering" of spots. As the size decreases and the number increases still further, these small spots begin to assemble on a series of concentric rings. Finally the spots become so small and numerous that they merge into uniformly intense concentric rings, the so-called "powder" pattern. The maximum range of grain diameter over which these sharp rings are registered is from 10^{-3} to 10^{-5} cm. It is clearly evident that sharp interference effects can take place only with a certain minimum number of parallel diffracting planes in each particle. As this number falls below the minimum, or in other words, as the particle size decreases below about 10^{-5} cm., it follows that interference is less perfect and that the diffraction rings (or lines by the Hull-Debye-Scherrer method) will become broader in proportion to decreasing size until in the neighborhood of 10^{-8} cm. atomic dimensions are reached. These will merge and the pattern would be classed as amorphous. A measurement of line-breadth in the colloidal range will therefore enable calculation of particle size as will be illustrated later. The question arises as to how small a particle can be and still produce a diffraction pattern upon which maxima may be detected. Levi in his study of metallic catalysts reports that particles only about five times as large as the unit crystal cell (in other words, 10 or 15 parallel planes) will produce resolved diffraction maxima, even though these are very diffuse.

Now it must be noted that diffuse diffraction maxima must be the consequence of any crystal grating which is imperfect in the sense of having too few parallel planes, or of having these planes, ordinarily sufficient in number, distorted, bent or imperfectly aligned. In other words, it is conceivable that an assemblage of fairly large colloidal particles might yield very diffuse patterns simply because molecules which may themselves be very large are not oriented in regular fashion. This condition is observed in the colloidal gels and is particularly interesting in the light of the prediction that simple mechanical stretching might tend to pull these diffracting units into parallel position and thus permit them to act as a diffraction grating.

The question which naturally arises next is whether there is a continuous transition between crystaliine and amorphous state. From what has been said concerning continuous broadening of lines till these merge and spread over the entire film, such a process would be indicated. Sir William Bragg quotes the experiment by the present writer on carbon. An activated charcoal producing an essential amorphous pattern had certain characteristic chemical and physical properties which changed over to those of graphite upon brief heating at 1,100° C. The X-ray pattern, however, was unchanged since no lines appeared. The great activity of the original charcoal was ascribed to the free valences of disorganized carbon atoms. Upon heating, the solid phase being retained throughout, these began mutually to attach themselves to satisfy these bonds and to form crystal planes of graphite, which were still too few and bent to permit interference of rays, though the properties were typical of graphite. This stage of elementary organization was designated "*paracrystalline.*" Upon further heating the grains grew in size, and the planes in number and rigidity, so that broad diffraction lines for colloidal dimensions finally sharpened to the typical graphite spectrum.

Another state of affairs, however, is observed with those substances so masterfully studied by Friedel in Volume I of this work, which display mesomorphic states of matter or liquid crystal phases. Here there are sharp discontinuities between the liquid or so-called amorphous phase (though this yields liquid rings), the nematic (in which the long molecules point in one direction but are not constrained in parallel planes, hence produce no crystal patterns), the smectic (in which the molecules are arranged in parallel planes in one direction, thus giving a crystal interference for one dimension only), and finally the crystalline in which the molecules take up regular marshalling in three dimensions. Undoubtedly then, transition phenomena must occur in all cases of solidification of a molten substance, but only in the case of certain long organic molecules is the temperature range of each state sufficiently extended to permit detection and examination.

Grain Size Measurement in the Colloidal Range.

The measurement of particle size, particularly in the range 10^{-5} to 10^{-8} cm., is now a well-established application of diffraction information. In the colloidal range, the smaller the particle and the fewer the diffracting parallel planes, the less perfect is the sharply unidirectional interference of secondary waves, and the broader will be the diffraction maxima which characterize a given crystalline structure. Hence a measurement of the breadths of diffraction lines or spots at points of half-maximum intensity, leads to an evaluation of grain size in an aggregate or colloidal dispersoid.

Debye and Scherrer were the first to derive an equation connecting particle size with an experimental measurement of the breadth of interferences at points of half maximum intensities. The equation is

$$B_{\text{Scherrer}} = 2\sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\lambda}{D} \cdot \frac{1}{\cos\theta/2} + b = 0.94\frac{\lambda}{D} \cdot \frac{1}{\cos\theta/2} + b.$$

where B is the breadth of a diffraction interference at points of half maximum intensity, λ is the wave-length, D is the edge-length of the crystal considered as a cube, θ is the angle of diffraction and b is the natural minimum breadth of the Debye-Scherrer diffraction line which is a constant depending upon the particular apparatus and size and absorption of the specimen. Scherrer first determined b by plotting measured values of B against $\dfrac{1}{\cos\theta/2}$ for a sample of colloidal gold. The straight line drawn through the points was then extrapolated to cut the ordinate axis which was the value of $b_o = b_r$, where r is the radius of the camera. This equation served for several years though comparatively little work was done on critical experimental test. Selyakov, by a considerably more straightforward proof, derived the equation

$$B_{\text{Selyakov}} = \frac{2\sqrt{3\ln 2}}{\pi} \cdot \frac{\lambda}{D} \cdot \frac{1}{\cos\theta/2} + b$$

which differs from the Scherrer equation by less than 2 per cent. W. L. Bragg by remarkably simple reasoning and calculation utilizing the conception simply of n planes of thickness d arrived at the equation

$$B_{\text{Bragg}} = 0.89\frac{\lambda}{D} \cdot \frac{1}{\cos\theta/2} + b.$$

In 1926 von Laue [1] deduced from vector analysis a new equation which in its most general form is free from the limitations of the cubic system, and permits size evaluation in different directions and thus *shape* of a particle. In the simplest rigorous form this equation is

$$B_{\text{Laue}} = \frac{\frac{\pi}{2}\frac{\omega}{\eta}\left(\frac{r}{R}\cos^2\frac{\theta h}{2}\right)^2}{\sqrt{1+\left(\frac{\omega r}{\eta R}\cos^2\frac{\theta h}{2}\right)^2}-1}$$

where

$$\omega = \frac{1}{1.8} = 0.55;\ \eta = \frac{\omega}{2\pi}\,(B\cos\theta/2 - 1/B)\left(\pi\frac{r}{R}\right)^2\cos^3\theta/2;$$

r = radius of the cylindrical specimen. R = radius of camera and θ = reflection angle. A simplified expression used with singular success by Hengstenberg and Mark [2] in determining the actual size and shape of the colloidal micelles of rubber and cellulose is

$$R\eta = 0.088\,[(b\cos\theta/2 - (1/b)\pi^2r^2\cos^2\theta/2]$$

where $R\eta$ and θ have the same significance; $b = BR$ is the actually measured breadth of the interferences, and $\eta = \lambda/4\pi m a_i$ ($= \lambda/4\pi D$ for cubic crystals); where ma_i is the extension of the crystal particle in the direction a_i, or the magnitude which is to be calculated with all other numbers known or experimentally measurable. For the cubic system the equation reduces to the form $B_{\text{Laue}} = 0.90\dfrac{\lambda}{D}\dfrac{1}{\cos\theta/2} = + b.$

The Laue derivation has been subjected to critical examination and extension lately by Patterson,[3] Brill [4] and the writer. The necessary conditions for the Laue equation are for absorption in the crystal powder which is negligibly

small, for completely random orientation, for particles of the same form and size, for undistorted lattices, and for known crystal structures. Patterson extended the theory to the case where the particles have different sizes and showed that the sizes must have a Maxwellian distribution, while Mark favored a symmetrical distribution of the Gauss type.* Without information concerning the distribution function, the average particle size cannot be determined. Brill extended the theory to the case of substances opaque to X-rays, and derived corrections for absorption and for the overlapping of the α-doublet interferences.

The latest and most ingenious advance in particle size measurement has been made by Brill and Pelzer.[5] The previous methods have all been subject to uncertainties concerning the relation between blackening of the photographic film and the intensity of incident X-rays, and the determination of positions of half-maximum intensity of diffraction interferences by means of the photometer. If the specimen under examination is in the form of a hollow cylinder (and thus is transparent to X-rays and obeys the Laue equations), then over a certain range of particle size each interference will be split into two maxima, the separation of which is a measure of particle size. Instead of measuring breadth at points of half-maximum intensity, the much more direct measurement of the distance between two lines is involved. For both large particles yielding sharp interferences, and for very small particles for which these two maxima become broad and overlap, single lines are observed. The simpler equations derived for the particle size involved in the split lines are as follows:

$$\text{(Small)} \quad \eta = \frac{\cos \theta/2}{1.8 \,.\, \sqrt{2}} \sqrt{\left(\frac{r}{R} \cos \frac{\theta}{2}\right)^2 - \frac{7}{80}\left(\frac{e}{R}\right)^2}$$

$$\text{(Large)} \quad \eta = \frac{1}{1.8}\,\frac{1}{2}\sqrt{3}\,\frac{r}{R}\left[\cos^2 \frac{\theta}{2} - \left(\frac{e}{4r}\right)\right]$$

where e is the linear separation of the two maxima. Rigorous comparative tests have been made for the new equations derived for hollow cylindrical specimens, with complete agreement for magnesium oxide and electrolyte nickel containing sulfur (Brill and Pelzer) and even for preparations of colloidal gold, silver and carbon (Clark and Zimmer). Complete curves based on the Laue equations, with which particle size may be quickly determined, have been published by Brill and Pelzer.

Direct Measurement of Colloidal Particle Sizes.

The foregoing methods of particle size measurement obviously involve assumptions and independent methods of evaluation are necessary for their test. The best possible method would, of course, depend upon actual diffraction interference corresponding not to the small unit crystalline cells but to the length and cross section of colloidal particles, for each of which d may be calculated by the simple Bragg equation. This necessitates a regular arrangement and uniform size of these colloidal particles with respect to each other, so that specimens are limited to organic micellar systems consisting of small elongated particles regularly oriented in a fiber, such as in natural cellulose and in stretched rubber. Another difficulty naturally is that the diffraction interferences corresponding to colloidal dimensions of one or two hundred A.U. will appear at such small angles, that resolution from the primary un-

* This has been substantiated by Murdock.

diffracted beam will be extremely different or impossible. There are two experimental possibilities: define the beam by extremely fine pinholes or slits, or else utilize X-radiation with a wave length much greater than that usually employed (molybdenum $K\alpha$ doublet 0.71 A.U.; copper 1.54 A.U.). By the first method with copper radiation Mark [6] was able to distinguish a broad interference spot very near the primary beam for bamboo and wood cellulose, corresponding to a spacing of between 50 and 100 A.U. and evidently due to reflection from the surfaces of particles of this breadth. Clark and Corrigan [7] have utilized the second method with interesting preliminary results. A combined X-ray tube, pinhole system and camera was constructed with the target of the tube magnesium ($K\alpha$ wave length 9.86 A.U.). On account of great absorption of radiation, the entire apparatus was operated at the X-ray tube vacuum, and extremely thin specimens of rubber and cellulose employed. Upon the films appeared a ring for unstretched rubber corresponding to 99.3 A.U. and for cellulose fibers the spacings 85.0 (evidently corresponding to Mark's value for breadth), 274.1, 168.0 and 156.0 A.U. The micellar sizes deduced from measurement of interference breadths and calculation by the Laue equation, are approximately 50×600 A.U. for cellulose and $150 \times 500 \times > 600$ A.U. for stretched rubber. Further researches by this important direct diffraction method will permit a careful comparison of values and establish the validity of the equations deduced from theoretical considerations, which may then in turn be used with confidence for those colloidal substances in which there is no organized micellar structure.

Results on Colloidal Metals and Inorganic Compounds.

Numerous references are to be found in the literature to experimental measurement of particle size for colloids as well as identification of crystallographic system. It is convenient to determine these properties as functions of various methods of preparation of industrial materials. Citation of only a few examples must suffice here.

1. First of all, the identification of the colloidal state as molecular or super-colloid state (not limited to solutions as is the Tyndall cone).
2. Relation in grain size and structure in extremely thin electrodeposited films and colloidal sols, such as those prepared by the Bredig arc method.
3. Catalytic activity, as for nickel hydrogenation and dehydrogenation catalysts, as a function of lattice structure and grain size (work in the writer's laboratory indicating an optimum rather than minimum grain size associated with greatest activity).
4. Structure and grain size of colloidal lead as a function of therapeutic value when injected into tissues subsequently irradiated with X-rays.[8]
5. Structure and grain size as functions of spreading, wetting, obscuring power, stability, gloss, etc., and of method of preparation in pigments (zinc, lead, tin, aluminum and other oxides).
6. The discovery of the presence of colloidal crystallites in glass, entirely apart from coloring agents added.[9]
7. Grain size measurements in tungsten for electrical contact points and other metals where grain boundaries are not satisfactorily developed for microscopic counting even for large grains.
8. Studies of possible allotropic forms of colloids produced at various conditions of pH (in all ranges the sphalerite lattice and not the wurtzite is found for colloidal zinc sulfide, contrary to various contentions).
9. Numerous cases of identification of colloidally dispersed phases in natural and artificial minerals, alloys, including martensite and troostite, etc., uniformly mixed or at grain boundaries; clear differentration between solid solution and physical mixtures.
10. Test for presence of invisible colloidal particles, such as brass or copper in parchment; completeness of filtration and dialysis.
11. Grain size and uniformity (particularly barium), in metal mirrors, in radio tubes, photoelectric cells, etc.

12. Identification of adsorbent films and chemical changes (for example mercuric chloride solution adsorbed on charcoal gives the crystal diffraction pattern for colloidal mercurous chloride).

13. Studies of the phenomena involved in dyeing of textiles utilizing metallic sols adsorbed on fibers (sometimes fibered layer, sometimes random).

14. Estimation of crystallinity, dispersion and grain size of excess sulfur in vulcanized rubber.

15. Classification of amorphous carbon, coal, and resins.

Recently a series of papers have appeared from the laboratory of Sir C. V. Raman, which have advanced to a remarkable degree the knowledge of the structure of materials usually classed simply as amorphous. This has been made possible by the observation of an entirely new phenomenon appearing at small angles to the primary beam in the diffraction patterns of all varieties of amorphous carbon, namely, a strong scattering extending to about 7°. This corona was first observed in solutions of cane sugar and was definitely attributable to the molecules of the dissolved substance which are distributed at random in the solvent, much in the same way as gaseous molecules.

Krishnamurti [10] has found for samples of sugar, benzene, and naphthalene charcoals and carbon obtained by charring ash-free gelatin with molten sodium, together with colloidal graphite prepared by exploding graphite acid in a vacuum, that all showed the small angle scattering in a marked manner. The patterns showed two rings in addition to the central scattering, the first and prominent ring corresponding to the (002) reflection of graphite, having a spacing of about 3.8 A.U. as compared to 3.4 A.U. of graphite. The outer ring was fainter and broader and showed a spacing of 2.12 A.U. comparable to the (111) spacing of graphite (2.06 A.U.). The observations accord with the idea that in the amorphous state the carbon atoms join together in clusters, forming highly anisotropic units, essentially two dimensional, the thickness being about ⅓ the length or breadth. Assuming that the central scattering is due to the dimensions in the plane of the particle, and the first ring to its thickness, a rough calculation gives about 60 atoms of carbon per unit. This picture of the carbon particle agrees with chemical evidence, mainly its oxidation to mellitic acid and adsorptive properties.

Mahadevan [11] has made an extensive X-ray study of the various varieties of coal, principally vitrain and durain. Vitrain, for example, gives two halos in the position of the two most prominent graphite carbon rings. They are wide and diffuse, suggesting the colloidal nature of the diffracting particles. The halos are due to the complex carbon molecule present in vitrain. The increase of moisture content seems to be accompanied by a finer division of the particles as evidenced by broadening of the rings. The results on durain indicate that it belongs to a colloidal system of the suspensoid type, where vitrain acts as a dispersion medium and the ash and vegetable detritus (with free carbon as end product) as disperse phases. In a study of vitrains of different geological ages, the intensity of the general scattering is seen in the case of the older coals to be approximately proportional to the sum of moisture content and volatile matter. In all cases the sizes of the diffracting particles are found to be of colloidal dimensions.* The mineral matter studied in the ash is also present in a colloidal state. These and related investigations have opened up a whole new series of applications of the X-ray diffraction method by amorphous solids. There has been a further extension to the case of natural and fossil resins [12] and to the changes during heating of ordinary rosin, shellac and synthetic resins.[13] The importance of these studies can

* Thomas Graham, in commenting on the analogy between caramel and anthracite coal, said: "Caramelization appears the first step in that direction—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages." (*Phil. Trans.*, 1861, p. 216.) J. A.

scarcely be overestimated, on account of the much greater amount of information obtained on seemingly hopeless materials and on account of the possibility of solving many difficult problems, particularly in chemistry and geology.

The Nature of Colloidal Solutions as Revealed by X-Ray Diffraction.

Following the discovery of Krishnamurti [14] that diffraction pattern of aqueous solutions of cane sugar, levulose and glucose were distinguished by intense scattering at small angles due to the dissolved molecules, it was then possible to undertake the study of colloidal solutions for which the state of molecular aggregation has been the subject of much speculation. The molecular weight of dextrin calculated from the extent of "amorphous" scattering by means of the Bragg formula $n\lambda = 2d \sin \Theta$ comes out 600, and for gelatin, 3,000, which are not improbable values. The solution of sodium oleate produced a ring due to the presence of big groups or micelles of sodium oleate in the solution. The extent of the gaseous scattering gave the dimension for the sodium oleate molecule, agreeing with that calculated from molecular weight and density. An excess of scattering directly adjoining the central spot, is due to big groups of ionic micelles described by McBain. Aqueous solutions of starch, tannic acid and gum arabic showed a further scattering at small angles to the primary beam, due to the dissolved molecules or micelles. The molecular weights calculated from the extents of the coronas were 6,200, 3,134, and 2,810, respectively. Thus, a starch molecule contains about 10 dextrin molecules united together, and a tannin micelle contains 10 simple molecules of the formula $C_{14}H_{10}O_9$. The great importance of these studies is at once apparent, when it is considered that extremely valuable information should be obtained from biological fluids including blood, filtrable virus, etc. In all these cases of amorphous solids, liquids and solutions, the X-ray patterns are characteristic in showing the presence of one or more diffraction bands, even though these may be ill defined. The purely amorphous scattering where no maxima are present, evidently can exist only in the case of ideal gases. All of these newer investigations are in agreement with the contention by the writer that such a material as amorphous carbon represents an intermediate state designated as paracrystalline, through which the atoms of carbon have to pass before obtaining the orderly arrangement underlying the graphite structure.

The Structure of Highly Polymerized Organic Substances Found in Nature.

Only a short time ago, very little could have been said upon this subject, not only from the X-ray diffraction point of view but even from that of chemical investigation. The new appearance of a book of more than 250 pages by Meyer and Mark,[15] bearing the title of this section, is in itself sufficient evidence of the amazing progress in the study of some of the most familiar natural materials. Impetus to these investigations was given to a large extent by the X-ray analysis of polymerized formaldehyde in the laboratory of Staudinger.

X-ray results on the colloidal polymerized natural products indicate clearly that a common structural plan is utilized for such widely different substances as cellulose, proteins of all kinds, chitin, rubber, gutta percha, balata and chicle. Long primary valence chains or macro-molecules are built up from a relatively simple molecular group (for example, dehydrated glucose residues in cellulose and isoprene in rubber). A bundle of these chains which may be 500 A.U. long, is held in position by secondary valence forces and constitute

the colloidal micelle familiar in diffusion and molecular weight experiments. From usual diffraction patterns, however, very much smaller periodicities and simpler constitution are directly measured. The explanation is found in the fact that the long macromolecules are spiral in character, and one turn in the screw axis is sufficient for a diffraction periodicity, since all other turns are exactly the same. Within the unit crystal cell, therefore, only a small number of the molecules of the parent monomer are found, instead of one or more of the actual long macromolecules. The information obtainable from diffraction patterns of the crystalline part of these natural products is as follows:

(1) Crystallographic system.

(2) Dimensions of the unit crystal cell and the number of monomeric molecules in each, from a known density value.

(3) Coördinates of atoms within the unit cell which demonstrate molecular shape of simplest chemical unit, and the bonding of these through primary valence bridges into polymerized chains with small periodicities due to screw axis of symmetry. These chains are further indicated by optical anisotropy and by the remarkable persistence during all kinds of chemical treatment, such as oxidation, mercerization, xanthogenation, nitration, acetylation of cellulose, vulcanization of rubber, etc.

(4) The length of the macromolecules or in other words of the colloidal micelle, and of the cross section, which is determined by the number of chains in a bundle. These magnitudes are ordinarily calculated from the breadths of the intensity maxima as explained in a previous section. It has been possible, however, in the writer's laboratory to measure these large spacings from direct diffraction interferences when sufficiently long X-ray wave lengths are employed, so that angles of diffraction will be in turn sufficiently large to permit resolution from the undiffracted X-ray beam.

(5) The arrangement of the micelles within the substance, whether random, or with a preferred orientation with respect to one direction, as in a fiber axis. In the latter case a pinhole diffraction pattern shows uniformly intense continuous concentric rings. As definite positions are taken up, intensity increases in certain places and decreases in others. Rings become arcs and then symmetrically arranged spots as the orientation is increasingly more perfect.

(6) In terms of all the foregoing types of information, the effects of chemical change, swelling and mechanical deformation, such as tension, can be followed and, of course, observed properties rationally accounted for.

It is not possible in this chapter to present in detail for this great class of colloids the X-ray data and the steps in interpretation, which have, it must be admitted, involved controversy, though not among X-ray workers.

Rather these results will be briefly tabulated and particular attention paid to the practical consequences and predictions from structural models constructed from X-ray data.

TYPICAL X-RAY DATA FOR FOUR IMPORTANT POLYMERIZED ORGANIC NATURAL MATERIALS.

Product						
Cellulose	Monoclinic	a	8.3	$4C_6H_{10}O_5$	C_2^2	50 A.U. cross
		b	10.22			600 A.U. length
		c	7.9			
		β	8.40			
Cellulose hydrate (mercerized)	Monoclinic	a	8.14	$4C_6H_{10}O_5$	C_2^2	Doubtful—chains less parallel
		b	10.30			
		c	9.14			
		β	6.20			
Rubber (stretched)	Orthorhombic	a	12.3	$8C_5H_8$	V_4	150 × 500 × > 600
		b	9.3			
		c	8.1			
Silk fibroin	Monoclinic	a	9.68			
		b	7.00			
		c	8.80			
		B	75° 51′	4 Alanylglycyl		

Consequences of Deduction of Structures.

1. **Cellulose.**[16] a. Proof of identity of crystalline part of natural varieties of ramie, sisal, jute, hemp, flax, cotton, wood, tunicin (animal cellulose), β cellulose (bacterial), etc.

b. Rational explanation of properties such as tensile strength, elasticity, etc., from arrangement of micelles: The more perfectly parallel to the fiber axis the greater the tensile strength.

c. Differentiation of cellulose fibers in terms of micellar arrangement (parallel to fiber axis in ramie, spiral layers in cotton) and of other substances present.

d. Surest method of identification of true cellulose, which involves *both* constitution and spacial coördinates: esterify unknown, dissolve in proper solvent, spin and regenerate fiber under tension to orient micelles, saponify in solid phase and examine diffraction pattern of fiber suspected to be cellulose.

e. A remarkable improvement in the quality of rayon from the prediction that tension on plastic fiber during regeneration should pull micelles parallel (X-ray fiber pattern) and greatly increase tensile strength; a structural test of every step in the process to yield optimum structure and properties; assurance that the manufacturing process has not been so severe as to break primary valence chains in original raw material (wood pulp or cotton linters), as was the case before X-ray research with micellar lengths only half as great as in starting material.

f. Improvements in cellophane manufacture to eliminate directional properties due to slight fibering in sheet when completely random arrangement is desirable.

g. Classification of raw cotton from degree of fibering since ultimate structure is conditioned by growth environment; proof that ancient cottons had a superior fibrous structure not now existent in any cultivated variety.

h. Study of growth of cotton daily from the root hair to mature 50-day fiber; diffraction patterns characterized by gradual increase in organization, decrease in lattice dimensions and hence intermicellar swelling and the sudden appearance of fibering with wall thickening.

i. Classification of kind of wood, angle of fibrils, differentiation of spring and summer wood, and of normal and compression wood (upper and lower side of bough).

j. A method of proving whether swelling is reversible and inter- or intra-micellar; for example wood and cotton swell when water penetrates between micelles: other solutions penetrate between chains and produce change in lattic dimensions; new processes for impregnation of wood to avoid swelling and water penetration.

k. A new process successfully predicted from cellulose model that cotton may be suitably swollen, maintaining solid form, stretched and greatly strengthened by virtue of improved orientation of micelles.

l. A proof that only the triacetate and trinitrate form definite crystalline substances, since esters of intermediate composition show X-ray interferences for unchanged cellulose and for the tri-ester only; for parts in which all of hydroxyl groups have not reacted, the distortion of the lattice results in no observable sharp interferences. On this account none of the commercial nitrate or acetate films yields more than a very diffuse amorphous pattern, so that variations in manufacturing steps cannot be followed; by plastic stretching of the films molecules are pulled more nearly into alignment, but only a pseudo-crystalline pattern and structure is gained before breakage on account of the interference of amorphous material with completely parallel orientation.

m. Discovery of the only method of obtaining native cellulose back from mercerized: two trinitrates are found from X-ray patterns, both produced from either native or mercerized cellulose under controlled conditions. Upon denitration Trinitrate I yields native, and II hydrated cellulose only.

n. Identifications of various compounds such as Knecht's (with nitric acid) Normann's (copper-alkali-cellulose), copper-amino-cellulose; a rational explanation of observed chemical properties and reactions, oxidation splitting, etc.

o. Conditioning of fiber structure to problems of dyeing, to various types of paper and a control of paper manufacture.

p. The proof that celluloid is a double compound of nitrocellulose and camphor. In a remarkably convincing series of papers,[17] Katz and associates have utilized X-ray patterns correlated with optical anisotropy to show that with small camphor contents (to 10 per cent) unchanged long nitrocellulose micelles and long micelles of the camphor-nitrocellulose compound lie side by side. The first possess strongly positive birefringence with respect to the longest axis, the latter weakly negative. The changes in diffraction patterns clearly indicate such a reaction with camphor, other cyclic ketones, acid amides and esters, aldehydes and nitriles (all predicted and verified from the observation of —C═O combination with nitrocellulose chain) as swelling and gelatinizing agents.

2. **Rubber.** a. Unique proof of micellar structure and parallel orientation of long-chain molecules of C_5H_8 when stretched.

b. A fundamental mechanism of elasticity based upon the mutual effects of double bonds in the unsaturated hydrocarbon in coiling up spring-like molecules are unheated.

c. A method of racking rubber 10,000 per cent or more, developed largely in the course of X-ray work.

d. Discovery that rubber after long standing at cool temperatures "freezes" and produces diffraction interferences for random crystal grains.

e. A "melting curve" for natural rubber determined by von Susich [18] from X-ray patterns. In frozen samples interferences disappear above 35° C., while with increasing degree of stretching the temperatures at which crystalline patterns became amorphous, increase up to 90° C. for great elongation.

f. The only exact method of distinguishing natural and synthetic rubbers so far produced, and the criterion of successful synthesis in the future—another indication that the terms rubber, cellulose, etc., imply not only constitution but also spacial structure.

g. Sharpening of interferences on vulcanization, indicating sulfur bridge formation between chains though the unit crystal cell is the same; with increasing sulfur content, loss of elasticity as a result of *net* formation of molecules in hard rubber.

h. Cooling of racked rubber with liquid air results in patterns with the appearance of Laue single crystal diagrams for metals, indicating larger organized lattice units than the usual micelle.

i. Rational explanation of greater tensile strength of stretched samples with greater van der Waals' forces; e.g. unstretched raw rubber (liquid air) 5.4 kg. mm.^{2}, stretched 35.1; vulcanized unstretched 5.3, stretched 44.4.

3. **Gutta Percha, Balata and Chicle.** There has been a very considerable disagreement concerning the structures of gutta percha and balata which are, like rubber, polymers of isoprene. The discrepancies have at last been explained in the work of Hopff and von Susich [19] and of Stillwell and Clark.[20] These two substances produce diffraction patterns different from rubber, but probably like each other. There are two modifications, the α which is stable below 60° C. and β produced by heating above 60°, giving different patterns in the unstretched state. The β-modification also produces a fiber pattern, since the specimens must be warmed before stretching. Stillwell and Clark have found balata in ordinary commercial form to differ from ordinary gutta percha, in the same way that von Susich's α-modification differs from β-gutta percha.

Chicle has been studied by Stillwell and Clark. The hydrocarbon constituent here is identical with gutta percha. The resins, calcium oxalate and other substances constitute the remainder of this product.

Rubber, gutta percha, balata and chicle all are built from hydrocarbon chains of the same constitution. The difference comes in a *cis* configuration for rubber where the identity period is 8.2 A. U. and a *trans* form in the gutta percha, or zig-zag chains with an identity period of 9.2 A. U.

4. **Proteins.** a. *Fibroin,* one of the constituents of natural silk, shows a distinctly crystalline structure, the analysis of which is given in the table. The chains of amino acid residues are bound in peptide linkage to form long spiral macromolecules, with 4 alanylglycyl residues per unit cell. The micelles are embedded in a matrix and are perhaps here and there chemically bound together. The amorphous part of the silk consists of irregular chains, which may even be bound into micelles, but without lattice arrangement. Such micelles are termed by Meyer and Mark "mixed micelles" by analogy with "mixed crystals." The great strength of the peptide chains and the bonds holding the micelles together are explained by the high mol cohesion of CONH (10,600), demonstrated by high heat of vaporization, high boiling point and high dielectric constant. A chain of 100 peptide residues (350 A. U.), as in fibroin, possesses a mol cohesion of over 1,000,000, very nearly the same as in a cellulose chain.

The micelles are resistant like cellulose to swelling media, in the sense of change of lattice dimensions. Swelling is, therefore, inter-micellar—a proof that within the micelle no free amido- and carboxyl groups exist. Only concentrated acids such as formic and some salt solutions swell the protein to the point of solution.

b. *Tendons, collagen, gelatin and tissues.*—The protein materials in natural fibrous form also produce fiber diffraction patterns. Stretched gelatin films approach the same structure, though never so perfectly crystalline evidently because the ends of the micelles are ragged. The identity period for tendon is 8.4 A.U., distinctly different from the value 7.0 in silk. A different arrangement of the chains is indicated, as is found for rubber and gutta percha. All properties indicate that a tendon is constructed similarly to racked rubber; heating causes contraction and disappearance of the fiber patterns.

Hence here again are long chain molecules in parallel orientation in bundles, a structure further verified by lengthwise splitting when frozen in liquid air.

Strength is obtained by such structure as shown by the fact that fresh tendon had a tensile strength of 11 kg./mm.^{2}; after contraction at 80° C., 3.0 kg./mm.^{2}; and after stretching back to the original length, 10.6.

Botanical tissues are webs spun from long primary valence carbohydrate chains, held by molecular cohesion of unsolvated groups or by chemical bridges. The chains may carry solvated shells on the polar or ionizable groups to account for the familiar freshness. Similarly animal tissues are webs of protein chains forming cell walls and accounting for combination with water. The most important difference between tissues, animal and plant, lies in the comparative non-elasticity of carbohydrate chains as compared with the pliable protein chain. Seifriz has stated positively as a result of the study of elasticity, that the last molecular entity of a living substance must possess an elongated form. Fibrous tissues, such as muscles and tendons, have principal valence chains parallel to the fiber axes. Tissue sheets, such as the fascia, have the chains in one plane.

The presence of distinctive larger, regularly arranged bundles of these long chains as micelles, seems clearly proved in cellulose, stretched rubber, silk fibroin, etc. In other cases, as in unstretched rubber and in tissues, the matter is not altogether settled. Studies of birefringence, of course, prove parallel orientation and these larger complexes can be demonstrated if the dependence of birefringence on imbibition of liquids with different indices of refraction shows a distinct minimum. The separation of birefringence due to the form of rod-like particles, as distinguished from that of single parallel long molecules (or characteristic birefringence), has actually been accomplished. It is not essential to give the name of *crystalline* to these conceptions of oriented long chains which actually diffract X-rays. A much higher degree of arrangement is implied by the term crystalline, since these long molecule chains still possess a rotational degree of freedom and hence are mesocrystalline or mesomorphic. For the first time, however, it is possible to attack the complex problems of chemical structures of chains, their positions in organs, the changes of their forms and position, the relation to each other and to the tissue fluidity. These have already been solved for the simpler fiber sections.

One problem to account for is the fact that many tissues which are insoluble in water still yield considerable quantities of protein to the solvent—a fact which demonstrates that the protein could not have been bound in a chemical network.

Przibram [21] has lately demonstrated by biological methods that the chromatin threads and even genes can be measured in length as 10^{-4} to 10^{-5}. The protein molecule is only one power of ten under the size of these powerful biological units.

Coming then to the behavior of living tissues, it has been demonstrated from mechanical and X-ray investigations that, in the extended muscle, the principal valence chains are in parallel orientation; in the contracted muscle, not. A muscle stretched and dried produces a fiber diffraction pattern, while a dried contracted muscle is amorphous, in keeping with the fact that the stretched muscle frozen with liquid air splits into shreds parallel with the fiber axis, while the contracted frozen muscle breaks into small clumps. von Hürthle [22] has shown that the birefringent part of the muscle fibrils is the actual contractile substance. This birefringence decreases with contraction; consequently the chains in the contracting fibril lose their parallel orientation. Until recently it has been impossible to prove whether or not this mechanism

is operative in truly living muscle. Experiments by Boehm and Schotzky [23] and by the writer,[24] utilizing the new high powered X-ray tubes which permit very rapid exposures, have thrown clear light upon this uncertainty. Diffraction patterns of living, electrically contracted frog muscle (excited by an applied voltage to tetanus contractions), have previously been procurable at a great sacrifice. As each muscle after killing the frog remains sufficiently fresh for only ½ minute in the path of an intense X-ray beam, several hundred muscles have been necessary. Diffraction patterns may now be obtained in 2 minutes with only six muscles. With the exception that the diffraction ring for water is present, the patterns are the same as for dried muscle. Contracted living muscles show a great decrease in fibering as compared with the muscle at rest.

A plausible mechanism for muscular action can be deduced in terms of inner molecular forces.[25] Rubber contracts because of double bonds in the long hydrocarbon chains which cause a spring-like coiling. In muscle protein there are many free basic and acid groups in the chains, since glutaminic acid and arginine and lysine may be derived. At the isoelectric point COO^- and NH_3^+ ions may attract and pull the chain into a close spiral.

In acid or alkaline media, however, COO^- or NH_3^+ ions repel each other and straighten out the chain. In confirmation of different chain configurations, casein and hemoglobin form the homogeneous layers in acid or alkaline aqueous solutions 7 or 8 A. U. thick, while globules only form on a neutral surface.

Hence contraction or expansion resides in the ultimate long chain molecule. Since these are bound together by molecule cohesion or bridges throughout the whole length of the muscle, an inner molecular change, with changing pH value, produces a contraction or expansion on the macroscopic scale. The physiological and chemical changes relating to production and destruction of acid in the muscle, therefore, lead to direct action on the protein chains and account for the mechanical work. The important conception of change in form of the protein chain as a function of the medium may, therefore, be extended to the behavior of protoplasm and to many physiological problems.

The foregoing account of the new knowledge of natural colloidal protein materials is sufficient to indicate the practical value of such methods of study. The changes in tissues shown by X-ray diffraction throw great light not only on physiological processes, but also on pathological developments. A detailed paper from the writers' laboratory shows how cancerous tissue (uterus, breast bones, etc.) produces characteristically different effects than the normal specimens, which may result in valuable diagnostic progress. A technological application is in the production of improved surgical catgut for ligatures and sutures. Here the process of swelling and tension, referred to so frequently, is highly effective in improving micellar orientation followed by the X-ray patterns, and tensile strength. The dispersion and respinning both of silk and of animal tissues is an accomplished procedure, and any desired properties can be obtained in terms of regulation of the variables. In other words, an inferior quality catgut can be vastly improved by these steps, just as cotton or rayon can be structurally changed and improved by swelling or dispersion and tension.

In conclusion it may be clearly stated that X-ray diffraction methods and research have already made a highly creditable contribution to the knowledge of structure and practical behavior of colloids of every type, from the simplest metal sol to the most complex living tissue. But the beginning only has

been made. New progress with this all-powerful vision of matter afforded to man by X-rays will undoubtedly surpass the most enthusiastic imagination.

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See also papers of P. P. von Weimarn in this volume, of G. Friedel in Vol. I, and of Alexander and Bridges in Vol. II of this series.

Wetting of Solids by Liquids

By F. E. Bartell, Chemistry Department, University of Michigan.

One of the most commonly occurring of phenomena is that of the wetting of solids by liquids. Processes involving wetting are encountered continually. Life itself is possible only because certain liquids are properly wetting the different solid constituents of the body. Important technical processes are fundamentally dependent upon the degree of wetting of solids by liquids. Since the process of wetting plays such an important part in our everyday lives, one must be impressed by the fact that but little data of a quantitative nature relative to wetting is existent in the literature.

There are many instances in which a difference of opinion exists as to whether a given liquid will wet a given solid; for example the following questions often arise: Will water wet paraffin? Will mercury wet glass? etc. There is lamentable lack of agreement as to what criteria should be accepted as an indication of wetting or non-wetting. Recently [1] an attempt was made to show that apparent differences of opinion were due not so much to actual differences in ideas as to differences in terminology used in the definitions and in the discussions. If wetting be defined as "*that phenomenon which occurs when a solid phase and a liquid phase come into contact in any manner, so as to form a solid-liquid interface,*" the ground for controversy relative to wetting and non-wetting has been removed. There remains only the question of *degree of wetting* of the solid by the liquid. If it be further specified that degree of wetting means the amount of change in free surface energy which occurs (or the work done by the system) when the solid and liquid are brought together, all confusion can be avoided. One must, however, consider carefully the precise manner in which contact is made between the two phases. Before contact both the solid and the liquid systems possess a definite amount of free surface energy. After contact, the system as a whole possesses a different but definite amount of energy, the amount depending upon the type of wetting.

It has been pointed out in a recent paper [2] that there need be considered three, and only three, different types of wetting. These have been designated as (a) *adhesional wetting,* (b) *spreading wetting,* and (c) *immersional wetting.* The terms are indicative of the processes employed to induce the wetting. With proper application of the principle underlying each of these types of wetting the apparent discrepancies existing in the literature disappear. Recently methods have been developed which make it possible to measure in terms of the absolute units, energy changes which occur during the different processes of wetting. It is believed that as experimental data becomes available, such data will prove to be of much value both in the furthering of fundamental researches in colloid chemistry and in the solving of technical problems.

Free Surface Energy.

Every surface or interface possesses free energy. In order to form new surfaces work must be done, i.e., energy must be expended upon the system. A definite quantity of this energy is converted into free surface energy.

Free surface energy is potential energy and the system is therefore in condition to do work. For a given type of system the total free surface energy is dependent upon the surface area; it follows then that processes which tend to decrease either the surface area or the magnitude of the free surface energy will tend to occur spontaneously.

Free Surface Energy of Liquids.

A surface may be defined as a boundary between two phases. In order to have two phases present in a system, at least one set of cohesive forces must be greater than the adhesive forces; otherwise, complete miscibility will result. In the case of a liquid in contact with its vapor or with air, a molecule within the body of the liquid will be attracted equally in all directions, while a molecule at the surface will be attracted more strongly toward the liquid than toward the gaseous phase. The surface molecules are therefore acted upon by an unbalanced set of forces, the resultant of which gives a tension at the surface. This tension operates so as to reduce the surface to a minimum. Accordingly drops of liquids tend to assume the spherical form. Consider a line 1 cm. in length on the surface, the force exerted in each of the two directions perpendicular to this, but parallel to the surface, is defined as the surface tension. For water at 25° C. the surface tension, S, is about 72 dynes. Assuming temperature constant, the operation of this force through unit distance, 1 cm., could result in the formation of a new surface of unit area, 1 cm.^{2} The work done in forming this new surface is equal to S (72 dynes) $\times$ d (1 cm.) $=$ 72 (ergs) $= S_e$, the free surface energy. Thus it is seen that the surface tension of a system is numerically equal to the free surface energy of that system, or $S = S_e$. The symbol, S, may then be used to indicate either the value of the surface tension or of the free surface energy of the system.

The methods for the measurement of surface tension of liquids are well known and will not be discussed.* From the foregoing it is apparent that if two surfaces of a given liquid, as water, be brought into contact, the surfaces will disappear. The free surface energy becomes zero and the work done (in the case of water) will be equal to 2×72 $(S) = 144$ ergs per sq. cm. of water surface eliminated. For a given pure liquid the work of cohesion, W_c, is numerically equal to twice the surface tension [8] or twice the free surface energy, i.e.,

$$W_c = 2S$$

When two different but miscible liquids are brought together the work of adhesion is equal to the sum of their surface energies. When, however, two immiscible liquids are brought together an interface results. This means that some free surface energy will still remain within the system and that not all the original free surface energies of the two liquids will have been expended.

Free Surface Energy of Liquid-Liquid Systems.

If benzene be shaken with water until fully dispersed throughout the water, and then be allowed to stand, the benzene particles will quickly coalesce and combine. The free surface energy of the benzene-water system is comparatively high and the system is correspondingly unstable. Coalescence causes a decrease of the surface area with a corresponding decrease in the free surface energy. The addition of a small amount of sodium oleate to the system before shaking will give a finely dispersed system of benzene in water which will remain fairly stable. Much of the sodium oleate will go to the

* *See* paper by W. D. Harkins in Vol. I of this series. J. A.

interface, for by this distribution the free surface energy of the system will be carried to a low level. The sodium oleate is said to be adsorbed at the water-benzene interface.

The behavior cited above is characteristic of heterogeneous systems in general, and of colloid systems in particular. Systems possessing high free surface energies are unstable and tend to pass to a state in which they can exist at a lower energy level. Such states can be reached either (a) through coalescence or aggregation of particles with attendant decrease in surface area, or (b) through adsorption of some component at the interface with resulting lowered surface energy.

The interfacial tension at liquid-liquid interfaces can be determined fairly accurately and without serious difficulty. Ferguson [4] has described a number of methods. Probably the most extensive and at the same time the most reliable data available at present is that which has been obtained by Harkins and co-workers.[5]

Free Surface Energy of Solids.

Solids differ from liquids in that their molecules possess less kinetic energy. When the kinetic energy of the molecules of a liquid is sufficiently lowered by cooling, the fields of force of the atoms operate so as to bring about a definite orientation of the molecules. This orientation results in crystallization. A solid is formed. A given solid in a specified medium possesses a definite interfacial energy against the medium. The discussion given above concerning the stability of liquid dispersions would apply with but slight modification to corresponding solid systems.

In order to cleave a crystal, a definite amount of energy must be expended. The energy expended must be sufficient to overcome cohesive forces, or to overcome the so-called lattice energy of the crystal. Subdivision of a crystal results in a corresponding increase in surface area, thus mechanical energy may be converted into free surface energy. Subdivision of 1 $cm.^3$ of a solid into particles of colloidal dimensions will increase the surface area about one million fold, likewise it will increase the free surface energy a corresponding amount. This accounts for the greater activity of the finely divided, or colloidal, material.

When a crystal is ruptured, cohesional forces responsible for the lattice framework are overcome. The surface is left chemically unsaturated. It possesses free surface energy. The lattice points may now function either as sources of "cohesional" forces or "adhesional" forces. The placing of a crystal in solution tends to lower its free surface energy. The extent of lowering depends upon the nature of the liquid in which it is placed. If the free surface energy is greatly lowered it means that a high attraction exists between the liquid and the solid. If this attraction be sufficiently high, the solid will dissolve in the liquid. If the attraction be less, some of the solid will remain undissolved and the system will then still possess free surface energy. This surface energy can be dissipated either through adsorption of a third component at the interface, or through aggregation of particles, which aggregation may occur either between like or unlike substances.

Wetting of Solids by Liquids.

It was pointed out in our introduction that a given process of wetting should be considered under one of the three possible classes, namely, adhesional wetting, spreading wetting, or immersional wetting. The necessity for distinguishing between the three classes will be made apparent from the following:

Adhesional Wetting.

The simplest type of wetting for study is that of adhesional wetting. Consider, for example, a solid in air having one face of a unit area. Suppose this face be brought into contact with a liquid. A solid-air interface with free

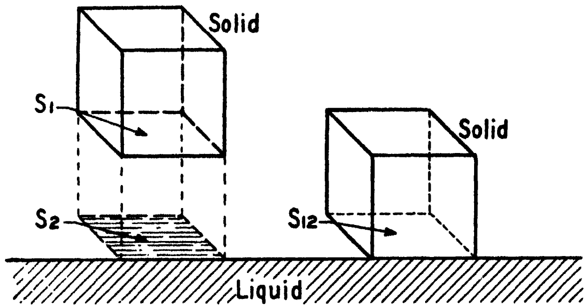

FIG. 1.—Adhesional wetting.

surface energy, S_1,* and a liquid-air interface with energy, S_2, will disappear. There will remain a solid-liquid interface with energy, S_{12} (Fig. 1).

The change in energy due to contact is $S_1 + S_2 - S_{12}$, or, as was first pointed out by Dupré,[6] the work of adhesion per unit area of solid can be represented by the equation

$$W_a = S_1 + S_2 - S_{12}$$

Spreading Wetting.

The work of spreading can be determined by considering the different free surface energy changes which occur during the process of spreading (Fig. 2).

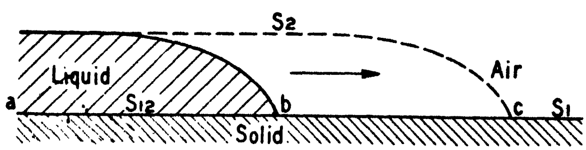

FIG. 2.—Spreading wetting.

Consider a drop of liquid in contact with a solid surface, *ab*. Assume that the liquid is caused to spread through distance *bc*, and that in so doing unit area of surface becomes covered. The surface changes which occur are:

(1) disappearance of unit area of solid-air interface (energy decrease $= S_1$)
(2) formation of unit area of solid-liquid interface (energy increase $= S_{12}$)
(3) formation of unit area of liquid-air interface (energy increase $= S_2$)

* The following symbols will be used to indicate surface tensions, interfacial tensions, and free surface energies.
S_1 = Surface tension of solid, or free surface energy
S_2 = Surface tension of organic liquid, or free surface energy
S_3 = Surface tension of water, or free surface energy
S_{23} = Interfacial tension of water-organic liquid, or free surface energy
S_{12} = Interfacial tension of solid-organic liquid, or free surface energy
S_{13} = Interfacial tension of solid-water, or free surface energy, etc.

The free surface energy changes involved are as follows:

$$\Delta S_G = S_1 - (S_{12} + S_2)$$

or the work of spreading

$$W_s = S_1 - S_{12} - S_2.$$

If a decrease in free surface energy occurs upon wetting, the liquid will continue to displace the gas from the solid, and if $S_1 > S_{12} + S_2$, the solid-gas interface will disappear provided there is sufficient liquid present to form a monomolecular film over it. In general it can be stated that in case the free surface energy at any one interface is greater than the sum of the free surface energies of the other two, the one interface will disappear.

Immersional Wetting.

Immersional wetting represents the work done in converting a solid-air system into a solid-liquid system.

Consider a solid of unit surface area in air. Its free surface energy is S_1. Immerse the solid in a liquid; its free surface energy is now S_{12}. The change in free surface energy, or the work of immersion is $W_i = S_1 - S_{12}$.

From the foregoing it is evident that when one refers to work of wetting, or energy changes accompanying wetting, one must specify the type of wetting involved. In adhesional wetting, the surface energy of the liquid aids in the process. In spreading wetting, on the other hand, energy must be added to the liquid surface in order that its area may be increased. It is then, in the latter case, correct to state that a high surface tension hinders in the process of wetting. Liquids with a low surface tension when placed upon a solid will wet the solid more readily and with less expenditure of energy than will liquids of higher surface tension. In the process of immersional wetting the surface energy of the liquid system remains in effect unaltered. When the process is completed, a solid-liquid interface has been substituted for a solid-air interface.

The formulations applicable to the different types of wetting are:

(1) For adhesional wetting, $W_a = S_1 - S_{12} + S_2$
(2) For spreading wetting, $W_s = S_1 - S_{12} - S_2$
(3) For immersional wetting, $W_i = S_1 - S_{12}$

The energy changes which occur in each case could be determined if the interfacial energy values represented in the different equations were known or could be measured. The surface tension values of a liquid, S_2, can be measured easily. Unfortunately, no satisfactory methods are known for the determination of either the surface tension of a solid, S_1, or the interfacial tension of a solid against liquid, S_{12}. Fortunately, however, the use of Young's equation [7] makes possible the determination of the value of $S_1 - S_{12}$. This is numerically equal to the work of immersion. Having this value, both the value for work of adhesion and work of spreading can be obtained, since the value for S_2, the surface tension of the liquid, is the only other value needed in each case.

Adhesion Tension.

Over a hundred years ago (1805) Thomas Young [8] published an *"Essay on the Cohesion of Fluids."* Although this article correctly outlined the principles fundamental to the measurement of degree of wetting of solids by liquids, but little constructive work of a quantitative nature has been carried

out along that line. He derived an expression for the equilibrium conditions existing in a solid-liquid system in terms of the contact angle and the different interfacial tensions. In terms of our symbols his expression is

$$S_1 - S_{12} = S_2 \cos \theta$$

which in words states that the difference between the interfacial tensions, solid-air and solid-liquid, is equal to the surface tension liquid-air times the cosine of the angle of contact. This equation has also since been developed by Poincaré [9] and by Dupré [6] and has been employed by a number of other investigators. The equation, though well known and entirely sound both from the standpoint of mechanics and thermodynamics, has not received the consideration it deserves. This is probably due to the fact that the existence of equilibrium contact angles has been the subject of debate and little reliable work on contact angles has been done up to this time. Very little data relative to contact angle values exists in the literature.

Freundlich [10] appears to have been the first to point out clearly the application of Young's formulation to degree of wetting. He suggested that the difference between the surface tension of the solid, S_1, and the interfacial tension solid-liquid, S_{12}, be designated as the *adhesion tension* (A) and that the value of this "is equal to the fractional part, given by the cosine of the angle of contact, of the surface tension of the liquid," i.e.,

$$S_1 - S_{12} = \cos \theta \ S_2 = A_{12}$$

It is probable that this formulation would have served as the basis of many researches had it not been for the fact that by far the majority of liquids form zero angles of contact with solids. In such cases the equation as given is indeterminate.

Within the past few years a method has been developed [11] which makes possible the determination of the adhesion tension of a liquid against a solid even though the two phases may form a zero angle of contact.

Method for Determining Adhesion Tension of a Solid Against a Liquid.

The method for the determination of adhesion tension of a solid against a liquid briefly summarized is as follows:

First some liquid must be found which will give an angle of contact with

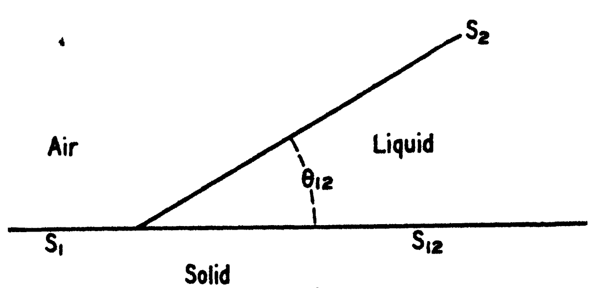

Fig. 3.

the solid under investigation. Having determined the angle of contact and knowing the surface tension of the liquid, the adhesion tension of that solid-liquid system is calculated by means of Young's formulation (Fig. 3).

Young's principle applies equally well to equilibrium conditions in liquid-liquid-solid systems (Fig. 4).

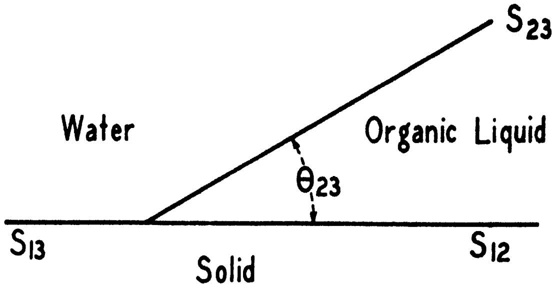

FIG. 4.

The formulation which applied is as follows:

$$S_{13} - S_{12} = \cos \theta_{23}.S_{23} = K_{23}S_{23}$$

By determining the cosine of the interfacial contact angle θ_{23}, or its equivalent, K_{23}, and the interfacial tension liquid-liquid, S_{23}, the difference between the interfacial tensions of the two different solid-liquid systems can be calculated since this value, $S_{13} - S_{12}$, is equal to the interfacial tension, S_{23}, times the cosine of the contact angle, i.e., $\cos \theta_{23}$.

Consider next the solid-liquid (liq. 3) system, the adhesion tension of which it is wished to determine. Assume this system to be one giving a zero angle of contact. Since angle θ is zero, the fundamental equation is indeterminate. But we may write:

$$S_1 - S_{13} = \cos \theta_{13}S_3 = K_{13}S_3 = A_{13}; \quad (1)$$

also

$$S_1 - S_{12} = \cos \theta_{12}.S_2 = K_{12}S_2 = A_{12}. \quad (2)$$

Combining these equations, we find

$$S_{13} - S_{12} = A_{12} - A_{13}. \quad (3)$$

But

$$S_{13} - S_{12} = \cos \theta_{23}.S_{23} \quad (4)$$

$$\therefore \quad A_{12} - A_{13} = \cos \theta_{23}S_{23} \quad (5)$$

The value for $S_{13} - S_{12}$ (or $A_{12} - A_{13}$) can be determined by means of equation (4), and the value for A_{12} (i.e., for a contact angle liquid) by equation (5). Accordingly, one can solve for A_{13}

$$A_{13} = A_{12} - (\cos \theta_{23} \cdot S_{23}). \quad (6)$$

The data necessary, then, for the determination of the adhesion tension of a liquid (liq. No. 3) which forms a zero contact angle with a solid are:

1. Surface tension value for liquid (2) — air $= S_2$.
2. Surface tension value for liquid (3) — air $= S_3$.
3. Interfacial tension value for liquid (2) — liquid (3) $= S_{23}$.
4. Contact angle values for liquid (2) — solid — air $= \Theta_{12}$.
5. Contact angle value for liquid (2) — liquid (3) — solid $= \Theta_{23}$.

A number of researches have been conducted on the determination of adhesion tension data and some of the results obtained have already been published.[12, 13, 14, 15, 16, 17]

Energy Levels of Solid-Liquid Systems.

Adhesion tension values give a measure of decrease in free surface energy which occurs when a liquid replaces air or other liquid from a solid-air or solid-liquid interface. Since the energy at an interface tends to reach the lowest value possible, that liquid which will carry the system to the lowest energy level will tend to displace from the solid any other liquid or gas which exists in equilibrium with the solid at a higher energy level. Adhesion tension values thus give a measure of degree of wetting.

Since adhesion tension values represent the work done in passing from a solid-air system to a solid-liquid system, adhesion tension values are numerically equal to the work of immersion values, i.e.,

$$W_i = S_1 - S_{12} = A_{12}$$

In like manner it may be stated that work of adhesion is equal to adhesion tension plus the surface tension of the liquid, or

$$W_a = S_1 - S_{12} + S_2 = A_{12} + S_2$$

and the work of spreading is equal to the adhesion tension minus the surface tension of the liquid, or

$$W_s = S_1 - S_{12} - S_2 = A_{12} - S_2$$

Thus it is apparent that adhesion tension values give a satisfactory means for evaluating the different types of energy changes which occur when a solid becomes wetted by a liquid. In interpreting results, it is only necessary to keep in mind the precise type of wetting involved.

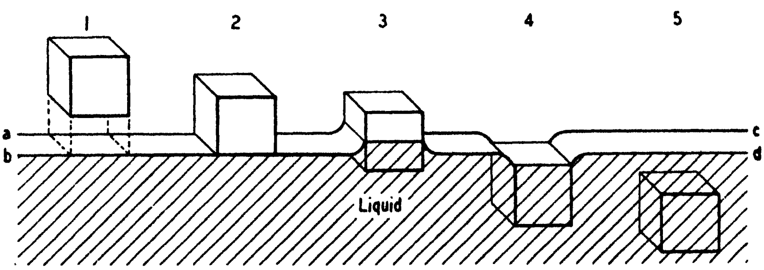

Fig. 5.

During immersion of a solid, each of the three types of wetting may be assumed to have occurred at some stage of the process.[18] Figure 5 represents the different stages which may be considered in the immersion of a solid in a liquid. In passing from 1 to 2 we pass from a condition of no wetting to the first stage which involves adhesional wetting, at stage 3 immersional wetting is occurring, while at stage 4 spreading wetting is about to occur. Thus in passing from stages 1 to 6 there is involved each of the three types of wetting.

Relation between Contact Angle and Type of Wetting.

A critical study of the three types of wetting will show that the relation between the angle of contact existing between the solid and liquid (*see* Fig. 6)

and the possibility of a particular type of wetting occurring unassisted is as follows:

1. Adhesional wetting is positive when the angle of contact is less than 180°. There appears to be no case in which this type is negative. Accordingly it should follow that any liquid will tend to wet any solid if the two are properly brought together (i.e., in a manner that will result in adhesional wetting; any solid when placed in contact with a liquid should be wetted by it).

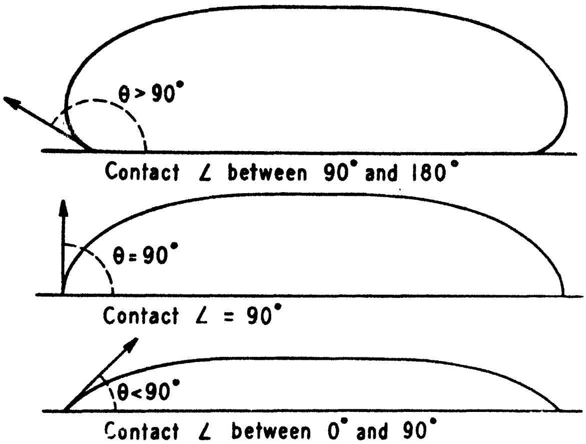

Fig. 6.

2. Immersional wetting is positive when the angle of contact is less than 90° and is negative when the angle of contact is greater than this value. This is in keeping with the fact that solids with contact angles less than 90° against a liquid tend to immerse themselves in the liquid. While, if the contact angle is greater than this, work must be expended upon the system to bring about immersion.
3. Spreading wetting is positive only when the angle of contact is zero, and it is negative for all larger values of this angle. Liquids will tend to spread out in thin films over solid surfaces only when the angle of contact is zero.

Wetting Power of a Liquid.

Many writers have argued that the "wetting power" of a liquid is determined by its surface tension. This statement is correct, but it is not correct to state, as has so often been done, that liquids with the lowest surface tension give the highest degree of wetting.

Liquids with a high surface tension possess high free surface energy. A portion of this energy will be contributed during the process of wetting provided wetting of the adhesional type is involved. In this type of wetting, other factors being equal, liquids with a high surface tension will produce with a given solid, the highest degree of wetting. It must be remembered, however, that high surface tension represents a high force of molecular cohesion and we have as yet no way of determining the exact relationship between available cohesional and available adhesional forces of any substance.

In the process of immersional wetting the question of surface tension of the liquid does not enter directly since no free surface energy of the liquid is contributed in the process.

In the case of spreading wetting, the question of surface tension is important. A high surface tension opposes spreading, for the process of spreading involves the formation of a liquid-air interface and the higher the surface

tension of the liquid the more energy must be contributed for the formation of new liquid surface.

Spreading can continue unassisted only when the surface tension of the solid is as great as, or greater than, the sum of the surface tension of the liquid and the interfacial tension of the solid-liquid system, i.e., only when

$$S_1 = S_{12} + S_2$$

or when

$$S_1 > S_{12} + S_2$$

which is equivalent to stating that spreading wetting is positive and spreading occurs unassisted only when the adhesion tension is equal to, or greater than, the surface tension of the liquid. In case $S_1 < S_{12} + S_2$ spreading will cease when a contact angle representing the equilibrium value for this system is formed.

Distribution of a Solid between Two Liquid Phases.

The distribution of a solid between two liquid phases is governed by essentially the same factors that determine the equilibrium conditions for solid-liquid-air systems. The principal difference being that in the former system the interfacial tension is a governing factor instead of the liquid-air interfacial (surface) tension.

In general it may be stated that when an insoluble powdered solid is added to a vessel containing two immiscible liquids, such as water and an organic liquid, and the vessel is shaken, the powder will go either to the water (liq. No. 3), to the organic liquid (liq. No. 2) or will remain at the interface between these two liquids.

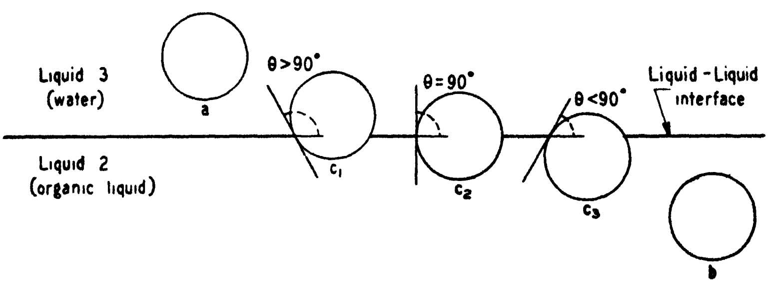

FIG. 7.—Distribution of a solid between two liquid phases.

In order to illustrate the application of the principles involved, let us consider the solid particle as a sphere in contact with the two immiscible liquids (Fig. 7).

Disregarding gravitational effects and considering only the influence of the different interfacial tensions within the system, the position of the sphere will depend upon the relative interfacial tension values of the system. The well-known relationships follow:

(a) If $S_{12} > S_{13} + S_{23}$, the solid will go completely to liquid No. 3 (*a* of Fig. 7).
(b) If $S_{13} > S_{12} + S_{23}$, the solid will go completely to liquid No. 2 (*b* of Fig. 7).
(c) If $S_{23} > S_{12} - S_{13}$, the solid will tend to collect completely at the interface (C_1, C_2, or C_3 of Fig. 7).

In case no one interfacial tension value is greater than the sum of the other two, the solid will remain at the interface, but will in all but exceptional cases (C_2) be wetted more by one liquid than by the other. The system may be said to be in equilibrium when

$$S_{12} - S_{13} = \cos \theta_{23} S_{23}$$

or when

$$A_{13} - A_{12} = \cos \theta_{23} S_{23}$$

i.e., when

$$A_{13} = A_{12} + \cos \theta_{23} S_{23}$$

Thus, in terms of adhesion tension, it follows that the greater part of the sphere will lie within that liquid phase which has the greater adhesion tension against the solid. The extent of passage into a given phase will be limited by the interfacial tension of the liquid system. Obviously the maximum free energy decrease of the liquid-liquid interface occurs when the equator of the sphere, that is its largest cross-sectional area, lies at the interface. As the solid becomes progressively immersed within one of the liquids beyond this point, additional liquid-liquid interface must be formed which requires energy for its formation. Some energy is contributed to the process by the wetting of the sphere by that liquid with the higher adhesion tension against it. Therefore, that complete possession of the particle by one liquid can result only in case its adhesion tension against the solid is greater than the sum of the adhesion tension of the other liquid against the solid, plus the interfacial tension of the liquid-liquid system.

These principles find extensive application in industry and their importance will become more pronounced as reliable adhesion tension data become available.

Some Applications of the Principles of Wetting.

It will not be possible, in this article, to discuss in detail all the fundamental principles underlying the wetting processes found in any one industry. Instead, an attempt will be made to indicate briefly a number of industries in which some of the principles outlined above do have direct and obvious application.

In attempting to classify the technical applications of wetting, it would seem logical to treat them under three principle heads, namely: a. Wetting processes; b. Non-wetting processes; c. Selective wetting processes.

Rigid treatment under any one of these headings is difficult, however, owing to the fact that a given process may involve the principles underlying each of the three classes mentioned. With this thought in mind at the outset, the reader will better understand some of the seeming inconsistencies in treatment which follow.

Processes Involving Wetting.

Numerous industrial processes involve the use of highly wetting liquids. In order to obtain the highest degree of wetting and at the same time the most complete wetting, the solid-liquid interface formed must be one with low interfacial tension, and in order to insure penetration into the interstices of the solid, the liquid itself must have a low surface tension.

Important principles relating to wetting are to be found in a study of *adhesives.** In the popular sense, adhesion is defined as the tendency to "stick," or adhere. In the cementing of joints there has been some question as to whether specific adhesion or mechanical adhesion is the more important factor.[19, 20] This question is as yet not fully settled.

* *See* paper on Cohesion and Adhesion by McBain and Alexander in this volume. J. A.

If two clean solid surfaces of a given substance could be brought closely enough together, they would adhere firmly. The trouble often encountered is due to the fact that the surfaces are not clean and cannot actually be brought into contact. Films of adsorbed material cover them.

Solid surfaces are often united by a liquid film placed between them. In order to obtain a firm and permanent union, the liquid should have a high adhesion tension against each of the solids and should solidify on standing. McBain and Hopkins,[21] from their study of adhesives, have concluded that any fluid that *wets* a particular surface and is converted into a tenacious mass by cooling, evaporation, oxidation, etc., may be regarded as an adhesive for that surface. These investigators, as well as Browne and Brouse,[22] have found that the joints formed with such adhesives are stronger than an equal cross section of the adhesive alone. The force of adhesion must in these cases be greater than the force of cohesion of the pure adhesive for itself. Likewise, it must be greater than the force of cohesion within the solid material. It is easy then to understand why thin layers of glue give a stronger wood joint than do thick layers.[23] The adhesive forces are assumed to predominate throughout the thickness of the film of the adhesive. It has been found, further, that adhesion is specific. Certain solids will give stronger joints with a given adhesive than will other solids.

A good *lubricating oil* should give good adhesion with metal bearings. Wilson [24] has suggested that certain liquids in contact with metal surfaces adhere so firmly that they may be considered to exist as plastic solid films.* The work of adhesion of liquid with the solid metal is in such cases much greater than the work of cohesion of liquid with liquid. Hardy [25] † believes that definite orientation of liquid molecules occurs at such solid surfaces. With a good lubricant the slip is believed to occur within the body of the lubricant midway between the two surfaces. Thus an oil of low viscosity may prove to be a better lubricant than one of higher viscosity. Molecules of fatty acids would show a greater tendency to become oriented at such interfaces than would less polar mineral oils. Wells and Southcombe [26] state that addition of fatty acids to mineral oils increases the wetting and thus improves lubrication. The fatty acids become adsorbed at the metal-oil interface; accordingly a very low concentration of such acids should be effective as a lubricating agent.

Upthegrove [27] has pointed out that "It is known that oils do not wet all metals to the same degree but that the degree of wetting occurs in the order of the adhesive forces" . . . "those metals which are wet to the greater degree by the oil are the ones which maintain the oil film over the surface" . . . "Greater resistance is offered to the breaking down of the oil film formed on some metals or types of crystal structure than on others" . . . "Experience has shown that the functioning of a plain bearing is dependent upon the extent to which true film lubrication is maintained, that is, it depends upon the nature of the solid and liquid interfaces and the extent and maintenance of them. Different metals, different oils will provide different interfacial conditions. With some metals the character and extent of the solid and liquid interfaces and the maintenance of them will be such that good bearing qualities will be provided. With others the opposite conditions will be found and the metals will have relatively poor bearing qualities."

According to Gibbs [28] "for given surfaces the lubricating power of a homologous series, e.g., fatty acids, is directly proportional to the molecular weight,

* *See* paper by Wilson in Vol. I of this series. J. A.
† *See* paper by Hardy in Vol. I of this series. J. A.

M, of the lubricant." Although the problems of lubrication are of great importance in this age of machinery, much work of a fundamental nature remains to be done. As yet there are available practically no data of a quantitative nature relating to the degree of wetting of metals by different liquids.

In *soldering processes* fluxes are used to displace impurities originally present on the surface. The flux must have high adhesion for the solid surface and must completely wet it.[29]

In the *glazing of pottery* the glaze must adhere firmly both in fused condition and after cooling.[30] That glaze which is best suited for one type of pottery will not, necessarily, be the best glaze for other types of pottery. Not only must the degree of adhesion of the glaze against the base be high but its coefficient of expansion must be about the same as that of the base. Ashley [31] has suggested that too great adhesion may cause cracking. This might, of course, occur in case there were too great a difference in the coefficients of expansion.

Advantage is taken of the fact that gelatin adheres strongly to glass in the manufacture of *pebbled glass.*[32] The adhesion is so great, that upon drying, the force of adhesion is greater than the force of cohesion of the glass for itself. Owing to the tension set up, glass is chipped off and attractive pebbled surfaces are formed.*

"Laminated Glass," such as is used for windshields in automobiles, consists of two sheets of glass between which is held some "non-breakable" material, such as celluloid.[33] Gelatin has been used as bonding material between the glass and the celluloid surfaces.[34] The surface of the celluloid may be peptized or may be treated with some other adhesive in order to effect a satisfactory bond with the gelatin, or in the absence of gelatin, with the glass itself. Inasmuch as the adhesion tension of water against glass is high, considerable difficulty has been encountered by the manufacturers of laminated glass in that water tends to creep within the plate and thus displaces the bonding material from the glass. In the process of glass lamination we have a good example of that type of wetting process which is known as "adhesional wetting."

Binding materials for *briquetting of coal* and charcoal possess as a main constituent some substance which has a comparatively high adhesion tension against carbon. They must be carbophillic in nature, i.e., must have properties in common with carbon. In this connection evaporated molasses [35] has been used as have also pitch and naphthalene.[36]

Sheppard [37] by means of a protective colloid prepared an emulsion of *pulverized coal* in oil.† The stability of the emulsion formed depended upon the degree of wetting of the "fixing oil." The interfacial tension of the "fixing oil" against coal powder must be low.

Sulfite liquors and other solutions have been used for *dust prevention.*[38] The main difficulty encountered in the wetting of the dust is due to a sheath of air (adsorbed) about the particles.[39] Solutions, in order to be effective for such purposes, must have a high degree of adhesion against the silicious material; they should also give a high and positive "spreading wetting." The plasticity of *ceramic materials* such as molding clays can be altered greatly by the use of liquids which give different degrees of wetting against the clay. An increase in the degree of wetting can in such cases be effected by inducing adsorption of some component at the solid-liquid interface. Alkalis and cer-

* Drying adhesive substances in beakers or dishes is apt to make much trouble in the laboratory, because the surfaces chip off. J. A.

† *See* paper on colloidal fuel in this volume. J. A.

tain salts of organic acids such as citrates and tartrates are readily adsorbed by constituents of the clays. The molding properties of clays can be altered greatly by the use of such solutes. In the "wet pan" method of clay wetting there is alternate compression and release of the clay as it passes under the mullers as well as continuous stirring by the scrapers.[40] These operations effectively remove entrapped air and bring about thorough wetting. The *plasticity of pastes* can be controlled to a great extent by regulating the degree of wetting of the dispersed solid by the liquid. As the degree of wetting is increased the interfacial tension solid-liquid is decreased; this tends to give a more fluid paste. Application of this same principle is of fundamental importance in connection with the technology of *dyestuffs,* of *paints* and *color varnishes,* and, in fact, is of importance in any industry in which pigments are used. Not only does degree of wetting determine the plasticity of pastes made from pigments, but it determines also the stability of the pigment when suspended in a liquid medium. The amount of pigment which can be incorporated into a paste having a certain specified body or flow characteristic is dependent upon the degree of wetting. Moreover, the degree of wetting determines largely the compactness of the mass which may form at the bottom of a container through the settling of pigment.[41] Difficulties due to "can settling" are often encountered in paints and varnishes which are allowed to stand for a long time on shelves or in storage.

Since each kind of pigment will give a different degree of wetting with a given liquid and also since a given pigment will give a different degree of wetting with different liquids, it follows that any given pigment-liquid system will tend to behave somewhat differently from any other.

The major processes of *dyeing* involve adsorption of dye material.[42] To insure uniformity in shade there must be uniformity of adsorption of the dye material. Accordingly the latter should be finely dispersed. "Aggregate crystallization" or cohesion of particles into flocs must be avoided. If dyes containing flocculates are used for printing, dark spots will be formed on the goods. This can be avoided by the use of proper dispersion media. Sulfonic acid salts have been used to lower the interfacial tension of such systems. The magnitude of the surface tension of the liquid medium is also important.

In the *grinding of pigments,* liquids should be used which have a high degree of wetting against the pigments. This insures a higher degree of dispersion of pigment. The successful *operation of colloid mills* likewise depends upon the careful selection of proper grinding media. In general, polar solids are highly wetted by polar liquids. Non-polar solids, such as carbon, are more highly wetted by the non-polar organic liquids.

"Seeding," one of the faults of carbon black varnishes, may be caused by the presence within the system of some impurity which has a high interfacial tension against the liquid. Traces of insoluble aluminum soaps will, for example, cause seeding.[43] Finely divided carbon black will collect at the interface insoluble soap-liquid. Through this action the originally higher interfacial tension is lowered. Seeding of this type can be prevented by having present some component (solute) which will be highly adsorbed at this interface.

Carbon pigments are used as a *filler for rubber.** Carbon gives an exceptionally high adhesion against the organic constituents of the rubber; this is desirable as it results in a product of high elasticity and good wearing qualities. Over one hundred million pounds of carbon black are used per year in the rubber industry alone. Large quantities of carbon pigments are used also in *printing inks,* in *stove polishes,* and in *shoe polishes.* In each of these

* Several papers in Vol. IV consider carbon/rubber relations. J. A.

preparations the liquids used must give a high degree of wetting with the pigment. In printing inks the liquid medium must possess a fairly low surface tension in order to give a smooth flow over the surface with a minimum tendency for the ink to pull up into drops; on the other hand "spreading wetting" (the magnitude of which is increased as surface tension of liquid is decreased) against the paper cannot be too high, otherwise a sharp imprint will not be obtained.

The *detergent action of soaps* is well known. Vincent [44] has made a thorough study of the importance of wetting as a factor in detergency. He concluded that concentrated solutions of soaps are good detergents because of their extremely efficient wetting and emulsifying ability. Soap solutions possess fairly high viscosity and low surface tension. This enables them to form stable films and foams.[45] Because of the tendency of the soap to be adsorbed at the solid interface, together with the attendant low surface tension and low interfacial tension of the solution against the solid surface, it can penetrate into fabrics. Owing to the higher adhesion tension of such solutions, waxes, oils and gums are displaced from cotton, wool,[46] and silk [47] by the solutions.

Soaps also have been used in the preparation of *horticultural sprays* and *insecticides* to increase the degree of wetting. The demands of such liquids are that they must wet and spread over the surface treated, they should give a high adhesion with the surface and should possess a low surface tension in order to insure spreading. It has been held that a low liquid surface tension was sufficient to determine the wetting power of a liquid; [48] that, we have seen, is not the case.[49, 50, 51] Vermorel and Dantony [52] have made a very careful study of this subject and have pointed out that the wetting power of sprays must not be confused with degree of adhesion. Casein and gelatin [53] have been added to spray solutions to increase the tendency to adhere and cover the leaves. Nuttall [54] has pointed out that "to compare wetting power by a determination of the surface tension of the wetting liquid only is misleading for two reasons: (1) The nature of the surface to be wetted is completely disregarded; (2) owing to surface concentration effects, the surface tension (static) of soap solutions does not vary with concentrations so diverse as 0.1 and 10 per cent (expressed as fatty acids), yet the wetting power of such concentrations differs greatly" . . . to wet well, a liquid "must possess both a low surface tension to air (S_2) and a low interfacial tension (S_{12}) to the solid to be wetted."

Non-wetting.

Processes carried out for the purpose of imparting non-wetting qualities to surfaces necessarily involve the principles of wetting and adhesion, for if a substance is coated over a surface to give non-wetting properties, that substance must in turn adhere firmly to the surface to which it is applied. In case the surface is carbophillic in nature, i.e., carbon-like, and possesses an attraction for organic materials (liquids), the problem is not difficult, as there are many organic water repellents which will firmly adhere to such surfaces. The problem becomes more difficult in case the solid material is hydrophillic in nature. Such a solid would have a high adhesion tension against water, but a low adhesion tension against the better known organic water repellents. The most effective coatings for such surfaces are those which, when cold, become hard and insoluble. Very few of our coating materials which contain volatile components are impervious to water after they have become set.

About the only paint or lacquer developed to date which appears to be strictly impervious to water is a form of rubber paint.

In general, in order to bring about conditions for non-wetting there should be a low degree of adhesion between the solid and liquid and at the same time the molecules of the liquid should have a high degree of cohesion with an attendant high surface tension. Many so-called "water-proofing" processes are known. The "non-wetting" qualities of *fabrics* and *cordage* are produced by impregnating these materials with insoluble soaps,[55] with paraffin,[56] with rubber, and with pitch coated with lamp black, graphite, etc. In each of these cases conditions exist which are most favorable to "non-wetting" by water, namely: (1) A high interfacial tension, S_{12}, exists between the impregnated solid and liquid (water). (This means also low degree of adhesion), and (2) Water is a liquid with a high surface tension (surface tension of water, $S = 72$ dynes).

If the work of cohesion, W_c, of liquid molecules for each other ($W_c = 2S$) is greater than the work of adhesion (W_a), of them against the solid, the liquid will not spread but will tend to pull up into drops which form an angle of contact with the solid. We know that work of spreading, $W_s = W_a - W_c$.[57] The work of spreading, W_s, is negative since $W_c > W_a$.

If, instead of water, almost any organic liquid were brought into contact with these surfaces, active wetting would occur and the liquid would spread. In this case the interfacial tension solid-liquid would be low, and the work of adhesion, W_a, correspondingly high. Furthermore, the work of cohesion, W_c, of most organic liquids is comparatively low, so $W_a > W_c$, and the work of spreading would accordingly be positive. While treated fabrics would not be highly wetted by water they would be readily wetted by organic liquids.

Solutions known as *anti-dimmers* have been applied to windshields, to the eyepieces of gas masks and to other glass surfaces to prevent accumulation of water droplets which impair vision. Perfectly clean glass would need no such treatment. It has a high adhesion tension with water and gives also a zero angle of contact which would eliminate drop formation. The difficulty is to keep glass clean. The liquid applied (for anti-dimming) is one which will adhere to the glass and at the same time give a low interfacial tension against water. Considerable work was done on this problem during the World War.[58, 59, 60] The function of the anti-dimmers is in fact not to prevent wetting but rather to insure a high degree of wetting (i.e., to prevent non-wetting) and thus prevent the formation of drops.

Attempts have been made to "waterproof" *building materials* such as *concrete, plaster, bricks, magnesite,* etc. The hydrophillic nature of these materials makes difficult the use of ordinary oil-bearing paints, for such paints have so high an interfacial tension against the surface they do not give good adhesion. In some cases it is true that preparations are used which do give a fairly high adhesion against these solids. It has been stated that void-filling substances[61] are better for such surfaces than "water repellents." Attempts have been made to incorporate water repellents, such as soaps, with the structural material.[62] It appears that one per cent or less of calcium or aluminum soap mixed with concrete does tend to make it waterproof.[63] *Paving materials* are waterproofed with certain asphalts and refined tars.[64] *Leather* is "waterproofed" by treating it with rosin, paraffin and tallow;[65] *wood* by treating with creosote oil; and *paper* by the use of insoluble soaps,[66] rosin,[67] paraffin and waxes. *Rubber trays,* used in the modern process of refrigeration, are used to prevent adhesion of ice to container.

Roasted coffee is coated with gums and oils to prevent absorption of water. Vita [68] has questioned the effectiveness of this treatment.

Lipsticks, alleged to "alleviate the discomfort of parched lips, due to climatic conditions," constitute at present a popular toilet article. The spreading and adhesive value of the base is supposed to be increased by addition of cocoa butter and the permanence or non-wetting property to the presence of stearic acid.[69]

Matches are coated with thin layers of such materials as beeswax, rubber cement, etc.[70]

Straw hats have been "waterproofed" by solutions of nitrocellulose and sandarac gums.[71] The gums give a high adhesion with the straw and at the same time give a fairly high interfacial tension against water.

Different *airplane dopes* have been tried with varying degrees of success.[72] Although spreading wetting against the coating may be negative, adhesional wetting is positive. Drops of water thus tend to adhere; if these freeze, additional layers of water readily adhere to the original ice drops and freeze, thereby forming a coating over the wings of the plane. As yet no entirely satisfactory material has been found.

The newly developed chlorinated diphenyl products give an exceptionally low degree of adhesion with water. These products should find important applications in non-wetting processes.[73] Halogen substitution products in general give a very high interfacial tension against water. While other examples of attempts to produce non-wetting surfaces might be given, the underlying principles related thereto would be similar to those mentioned above.

Selective Wetting.

The principles of selective wetting are applied to numerous processes involving separation and purification of materials. *Water can be separated from oil* by pouring the liquid on a fine mesh filter which gives a low interfacial tension against oil, but a high interfacial tension against water. Finely divided rubber, ferrous sulfide, and other materials have been used for this purpose. The oil which selectively wets the filter passes through leaving the water on the filter. Crushed calcium carbonate has been used to filter out *oils from water.*[74] It is more highly wetted by water than by oil. In this case oil is retained on the filter.

Silica gel has found quite extensive use in processes involving selective adsorption. Sulfur compounds are thus removed from petroleum oils.[75] Compounds which have a high degree of adhesion against silica can be readily adsorbed from liquids which have low adhesion against it.[76] Fuller's earth has also been used as an adsorbent in *petroleum refining.*[77] * Activated carbon finds extensive use in processes involving selective wetting (i.e., selective adsorption). The selective tendencies of carbon are very different from those of silica, in fact they appear to be quite opposite. Carbon is readily wetted by non-polar organic liquids but is poorly wetted by some polar liquids such as water. The reverse is true for silica. Recently an adsorptive material composed of a combination of carbon and silica has been shown to be unusually active in certain cases.

The *detergent action of soaps* has already been mentioned and has been ascribed to their selective wetting tendencies.[78, 79, 80, 81]

In the *de-gumming of silk,* liquids must be used which readily wet, soften and remove the adsorbed gums. Liquids are selected which have low surface

* *See* paper by Dunstan in this volume. J. A.

tension and high frothing power.[82] In the natural state *cotton* contains waxes and oils. This renders it non-wetting by water and a non-adsorbent to dyes. The oils can be removed by treating with dilute caustic solutions. The pure cotton fiber then readily adsorbs dyes.

Many effective *emulsifying agents* consist of finely divided solid, or semi-solid, substances.[83] When these are shaken with oil and water, a stable emulsion is formed. The type of emulsion which results is dependent upon the relative degree of wetting of the two liquids with the solid.[84, 85] That liquid which gives the higher degree of wetting will exist as the external phase, the other liquid as the internal or dispersed phase. Carbonaceous emulsifying agents tend to give water-in-oil emulsions while silicious materials tend to give oil-in-water emulsions.

Diamonds are recovered from blue sand [86] by mixing the sand with water and passing the mixture over shaking tables smeared with grease. The diamonds adhere to the grease, while the other constituents are carried off with the water.

Petroleum oils are recovered from oil-bearing sands by the so-called *water-flooding method.* To accomplish water-flooding, wells are drilled near the producing well (100 to 150 feet away); from these water advances through the sand displacing the oil, forcing it into the producing well. A number of investigators [87, 88, 89] have studied the relative effectiveness of aqueous solutions as flooding agents. Fyleman [90] found that dilute sodium carbonate appeared to be effective as a displacing agent. The ease with which an oil can be displaced from a sand depends largely upon the degree of wetting (i.e., the degree of adhesion) of the sand against the oil, as well as upon the degree of wetting of the sand by the displacing solution. Different crude oils have been found to possess very different degrees of adhesion against silica or sand.[91]

The *Trent process* for separation of coal from mineral matter involves a similar principle. In this process the crushed material is first mixed with water, then agitated with oil equal to about 25 to 30 per cent of its weight.[92] The coal is selectively wetted by oil and agglomerates. The mineral matter is selectively wetted by water, separates out, and is thus removed.

One of the most important of the industrial applications of selective wetting is that of the *concentration of minerals by flotation.* The process is generally applied to sulfide ores. Separation of metal-bearing sulfide particles from the gangue by flotation is ascribed to the fact that oils give a high degree of wetting with the sulfide constituents of the ore, while water gives high degree of wetting with the gangue. Much knowledge of an empirical nature relating to flotation of minerals is available though it must be admitted that but little constructive information of a strictly scientific nature is available. It has often been remarked that in this industry art has far out-distanced science. Edser,[93] Sulman,[94] and a few other investigators have attacked the problem from a theoretical standpoint. From their work it appears that a correct interpretation of the fundamental principles underlying flotation processes will come through a study of interfacial tension relationships of the systems involved. In connection with this study, a determination of contact angles and adhesion relationships of these systems should prove to be of great value not only in explaining the results obtained, but also in advancing the methods of the industry.

Many other applications of the principles of wetting could be cited. It is believed, however, that those mentioned will be sufficient to indicate something of the scope and importance of this phase of colloid chemistry.

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Spontaneous Dispersion of Small Liquid Particles

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We often observe the coalescence of two or more liquid drops into a larger mass. The inverse phenomenon, the spontaneous dispersion of a liquid mass into a number of smaller drops, is at first sight of a much rarer occurrence. However, closer consideration shows that in certain cases such a spontaneous dispersion does not represent anything exceptional. Thus, spontaneous emulsification consists essentially of a dispersion of a large mass of liquid into a great number of droplets of microscopic or submicroscopic dimensions, suspended in another liquid. Furthermore, cases of spontaneous division of liquid particles into smaller ones are not uncommon with liquid crystals [1] and myelinic forms.[2] The most interesting cases perhaps, where such phenomena occur regularly, are found in the domain of biology. Indeed the repeated fission of a cell exemplifies a periodical spontaneous division of a colloidal liquid system. This relative rarity of the phenomenon and its apparent inconsistency with the laws of capillarity makes a theoretical study of its possible causes particularly attractive.

If we attempt to establish some general theoretical bases for the explanation of this class of phenomena, we meet the following difficulty. A dispersion of a liquid particle is necessarily connected with an increase of its surface. But from the fundamental laws of capillarity, it follows that any liquid system with positive surface tension tends to acquire a shape which gives its surface a minimum area. For a free liquid particle this is a sphere.

At first sight one may attempt to assume the existence of a negative surface tension, which would tend to increase the surface of the particle as much as possible. Physically this is not an impossibility. For the surface tension of a liquid is the result of a one-sided attraction of the surface molecules by the inner molecules of the liquid. Now we may assume that the liquid particle is surrounded by another liquid, whose molecules attract the molecules of the particle more powerfully than the latter attract each other. A negative surface tension would thus result, and the liquid drop would tend to increase its surface. But such a stronger attraction of the molecules of the particle by the molecules of the surrounding liquid, physically means that the liquid, which constitutes the particle, is *soluble* in the surrounding one. Hence, the droplet will gradually dissolve and disappear.[3] In a certain sense we may say, that this is also a case of spontaneous dispersion, down to molecular dimensions; but it is not the kind of phenomena which interests us most. Spontaneous dispersion may occur also in cases of immiscible liquids, where the surface tension is positive.

The only logical solution of the difficulty is to conclude that when the liquid particle divides into two or several particles, and when the total surface thus increases, the surface tension, although remaining positive, decreases to a larger extent than the increase of the surface, so that the total surface

energy, which is equal to the product of the surface tension by the total surface, becomes smaller in spite of the increased total surface. This possibility has been considered first by Professor F. G. Donnan.[4] In other words, we must conclude that the surface tension of a smaller particle is less than that of a larger one.

Under what conditions is such a thing possible? This problem has been the subject of several publications of the writer,[5] a brief summary of which shall be given here.

If the liquid particle, which we shall call "drop," consists of only one chemically well-defined and perfectly homogeneous liquid, the surface tension is independent of the size of the drop. The free drop assumes always a spherical shape, which is the shape of minimum surface. No spontaneous division is possible.

However, if the liquid which constitutes the particle, contains in solution capillary active substances which have the property of lowering the surface tension of the solvent, the drop will no more be completely homogeneous. For the capillary active substance, according to a well-known theorem of J. W. Gibbs, will be adsorbed at the surface. In many cases, the inside of the liquid will be practically free from that substance, which will spread on the surface, forming there a monomolecular layer. As has been shown by the work of I. Langmuir, N. K. Adam and others,[6] such a monomolecular layer behaves like a really independent "two-dimensional phase," either liquid or gaseous. Thus the drop now consists of two phases—the "volume phase" and the "surface phase."

In the usual experiments on monomolecular films, the substance which constitutes the film (oil, fatty acid) does not combine chemically with the underlying solvent (water). In this case, the amounts of both solvent and surface-substance remain constant. A variation of the shape of the drop, which results in a variation of the area of its surface, does not change the physico-chemical constitution of the drop. The surface tension remains practically constant, and an increase of the surface results always in an increase of the total surface energy. Hence, only the spherical shape will be a shape of equilibrium, and no spontaneous dispersion is possible.

But once the existence of "two-dimensional phases" is established, a more general possibility must be quite legitimately considered. We may, then, consider the case of a reversible chemical reaction between the substance, which constitutes the "volume phase" and the one which constitutes the "surface phase." To give an example, suppose that the substance A, which constitutes the volume phase, is reversibly decomposed and in this way yields a substance B, which forms a monomolecular layer on the surface of A. In this case the relative amounts of A and B in the drop will, in general, vary if, keeping the total mass of the drop constant, we will change its shape and thus vary its surface. The concentration of B, per unit of surface, will no more vary inversely to the total surface, as in the previous case, when the total amount of B was supposed to be constant. This concentration will be a much more complicated function of the surface. And since the surface tension is a function of this concentration, the latter will also vary with varying total surface. Under certain conditions, specified mathematically in the papers referred to above, the surface tension may, with increasing total surface, decrease more rapidly than the total surface. As above stated, the total surface energy will in this case decrease with increasing surface, and hence the surface may increase spontaneously. The drop will spontaneously stretch and eventually divide in two or several smaller drops. For

a given volume of the drop, the total surface energy may have a minimum for a definite value of the surface. If this surface is larger than the surface of a sphere of the same volume, the drop must either divide into several smaller spherical drops, or else assume a non-spherical shape. Since, however, in this case we may vary the shape of a liquid particle in an infinite number of ways, without changing its surface, the shape of the drop remains to a certain extent arbitrary. It may be remarked, that this paradoxical fact of a liquid particle having a non-spherical shape may be observed on certain emulsions and "myelinic forms," for instance, on those obtained from lecithin in albumin solution.

As stated, the area of the surface, which corresponds to the equilibrium, that is, to the minimum of the total surface energy, is a function of the volume of the drop. If the drop grows on account of formation of its constituent liquid from the surrounding liquid, which may be of complicated composition, and if the equilibrium surface area grows more rapidly than the $\frac{2}{3}$ power of the volume, the drop cannot maintain its original shape: it will necessarily stretch, and under certain conditions, which are specified in the above-mentioned papers, it will gradually divide in two.

There is, however, also another aspect of the problem. Imagine a spherically shaped drop, consisting of a liquid A, which liquid is being formed by the combination of two other substances B and C, in such a way, however, that the reaction goes on at an appreciable rate only in the presence of A. (Autocatalysis.) If B and C are contained in the surrounding liquid, they will diffuse into the drop, and disappear there. There will be a concentration gradient of B and C in the drop, from the periphery to the center. Calculation shows that this gradient will be a function of the size of the drop. The drop is now again non-homogeneous, though this inhomogeneity is of a different nature than in the preceding case. The concentration of B and C at the surface will also be a function of the size of the drop, and therefore the surface tension, which is dependent on the concentration of various dissolved substances, will also be a function of the size. Under certain conditions, which are mathematically stated in the second of the papers referred to above, it may happen that, beginning with a certain size, the surface tension of the drop will be considerably larger than the surface tension of another drop of the same kind, but having only half the volume. If such a drop is divided in two halves, the total surface energy will become smaller in spite of the increased total surface. The large drop is therefore unstable, and a small disturbance will lead to a spontaneous division in two. The two halves, after having grown to a definite size, may divide again. In a more general case, we may consider not only substances which diffuse in the drop from outside, but also those which are formed in the drop as the result of different reactions and diffuse from the drop into the surrounding medium.

One particularly interesting possibility is to be mentioned in this case. If the drop has a non-spherical shape, the concentration along the surface will vary from point to point. Since the surface tension is a function of the concentration of the dissolved substances, the latter will also vary from point to point along the surface. In general, therefore, a non-spherical drop cannot be stable. But the distribution of concentrations and hence also the distribution of the surface tension along the surface, due to the diffusion, is determined by the geometrical shape of the drop. Now it so happens that for certain shapes, the distribution of surface tension is such that the product of the surface tension at a point with the mean curvature of the surface at the same point is the same for all points of the surface. Since this product

is equal to the capillary pressure, the latter is constant all along the surface, and the drop may be in equilibrium for this particular non-spherical shape. A detailed mathematical treatment of this case has been given by the author elsewhere.[7]

Another interesting conclusion is arrived at if we consider the *rate of growth* of such drops, and assume that besides the formation of the substance, which constitutes the drop, out of diffusing substances, a dissolution of this drop-substance takes place at the surface. In this case for very small drops, which have a very large specific surface, the second phenomenon prevails. The rate of growth is negative, the drop gradually dissolves and disappears. Beginning with a certain size and up, when the specific surface is already smaller, it is the first phenomenon, that of formation of the drop-substance, that prevails. The rate of growth is positive. The conclusion is this, that a drop can grow further only if it already has reached a certain size. It *cannot therefore be spontaneously formed* out of the surrounding solution, by a gradual increase from submicroscopic dimensions. But if in some way the drop is already there, and has a size above the critical, it may grow, and give rise to other drops by a process of spontaneous division, discussed above. For details we refer to the original paper of the author.[8]

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The Influence of Elasticity and Permeability on the Swelling of Two-Phase Systems *

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Purpose of the Investigation.

In his well-known paper on the laws of swelling, Katz [1] for the first time analyzed the relations existing between swelling-pressure, heat of swelling, relative vapor-pressure and volume contraction. The ideas developed by Katz still form the basis of present views on the nature of swelling, although some revision seems necessary. For instance, Katz believes that swelling is due entirely to physico-chemical reactions within the system, and ignores the purely physical factors which have a decisive influence on the process.

To estimate the importance of these neglected physical factors, we should examine the properties of coarse disperse systems and then proceed to gage the influence of an increase of the degree of dispersion on the behavior of the system. The properties of coarse disperse systems are wholly dependent on physical factors. As we proceed from coarse to fine disperse systems, the relative importance of the physico-chemical factors increases, due to their dependence on the specific surface, while purely physical factors, such as elasticity and porosity, remain as effective as before. A comparison of coarse and fine dispersed systems of the same chemical and morphological constitution will indirectly give an idea of the relative value of purely physical factors. The object of this paper is to illustrate the principle of this method, by giving a few examples, and to stimulate interest in research along the same lines.

Capillary Pressure and the Swelling Process.

Assume that the water content w_0 of a submerged two-phase system, which is covered by a filter is reduced to a value w_1 (per cent of dry weight) by an evenly distributed pressure p per unit area (Fig. 1a, volume reduction by aa' bb'). As soon as the external pressure p is removed, water will flow into the expanding system and its water content will gradually increase from w_1 to w_2.

The experimental procedure is then changed by reducing the water content to w_1 by drying instead of by applying the external pressure p (Fig. 1b) and we will assume that when the content is w_1 all the voids of the system are still filled with water—that is, no air has invaded the system. Finally the surface $a'b'$ of the system is flooded with water to initiate swelling as in the experiment represented by Fig. 1a.

If we compare the two processes represented by Figures 1a and 1b, respectively, the following facts emerge: Since swelling starts with the same quantity of water w_1, the arrangement of the particles (density of the strata and average amounts of particles per unit) is the same at this stage in both

* Translated by Mr. F. J. Zimmermann, New York.

cases. As in the case of Figure 1a a load of p per unit area of surface is necessary to prevent the gels from expanding, there must be a force of equal intensity acting on the surface $a'b'$ in the system shown in Figure 1b. This force is obviously exerted by the surface tension of the water, which the author terms "capillary pressure." The only difference between the two systems before swelling has set in, is that the interstitial water of the system represented by Fig. 1a is not under tension, whereas the water contained in the system represented by Figure 1b stands under a tension equal to the value p of the capillary pressure. Hence the solid phase is *in both cases* under the influence of a pressure p per a unit of area of surface which is transferred from the surface $a'b'$ through the particles to the bottom cd. This conclusion, based on fundamental laws of mechanics, conflicts with one of the conclusions drawn from Katz's theory of swelling. According to Katz, the "pressure of swelling is only exerted when the swelling process is arrested mechanically. Prior to this, it does not exist. It is also incorrect to say that water in a partly swollen body stands under such pressure.[2]

As soon as we remove the pressure p from the system (Fig. 1a), it begins to expand and to soak up water, i.e. to swell. Due to the low permeability of the system the removal of the external pressure p instantaneously produces in the interstitial water of the system a tension of the intensity p. This event

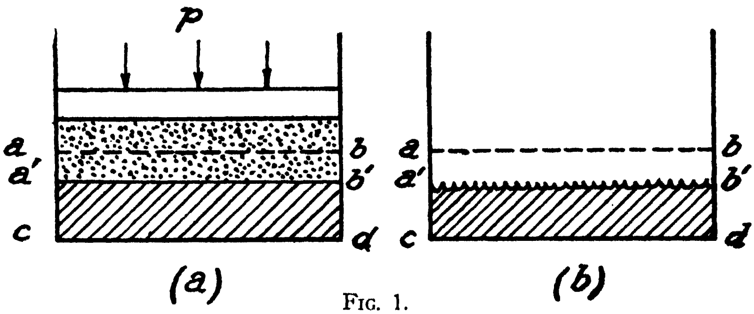


Fig. 1.

eliminates the only difference between the systems (Fig. 1 a and b). The difference between the pressure in the external water (free water) and in the interstitial water causes water to flow through the surface into the two-phase system until the hydraulic gradient disappears. The flow is identical with the flow of water through a pipe from one tank to another at a lower level, and is independent of the physico-chemical reaction inside the two-phase system. These conclusions are also based on the fundamental laws of mechanics.

Under these circumstances, the physico-chemical reactions, which according to Katz are the cause of swelling, must be considered as incidental. Water penetrates into a gel simply because of a difference in hydrostatic pressure, and physico-chemical activity is possible only *after* water has entered the system due to mechanical causes.

These considerations lead to the following conclusion: If, by evaporation, the water content of a two-phase system can be reduced from w_0 to w_1 which is above the transition point,* the same concentration can be obtained under water by superimposing a weighted filter. Under these conditions the following values are equal. the load (per unit of area) which is necessary to reduce the water content of the system from w_0 to w_1, the tension in the

* The transition point is the water content at which air enters the system.

interstitial water of the system concentrated by evaporation, and the swelling pressure, i.e. the pressure which is necessary to prevent the increase of the water-content of the system (swelling of the system), when it is flooded with water.

Heat of Swelling and the Lowering of Vapor Pressure.

When the two-phase systems represented by Fig. 1 begin to swell, water penetrates them owing to a difference in hydrostatic pressure in the external and internal water. The mechanical work is completely changed into heat because of the internal friction of the fluid flowing through the passages. This amount of heat can be calculated from the change of the relative vapor pressure,[8] provided that the change of vapor pressure is due only to the change of the radius of the menisci. By appropriate mechanical means, this heat can be converted into mechanical work.

Besides frictional heat, fine disperse systems generate heat by physico-chemical reactions. For instance, part of the water entering a swelling gel changes its physical properties, by forming an adsorption compound with the solid phase. Heat is also developed by the physico-chemical reaction between water and the solid phase. It has, however, not been proved that this heat can, like the frictional energy, be changed entirely into mechanical work. Indeed, it is difficult even theoretically to devise a means of converting this fraction of the total heat into mechanical energy. The heat evolved by the reaction of solid with liquid phase is fundamentally the same as the heat evolved by mixing two miscible fluids (say H_2SO_4 and water), which is associated with a contraction of the volume and the lowering of the relative vapor pressure. It is not possible experimentally to find out how much of the lowering of the vapor pressure is due to the change in curvature of the meniscus, and how much to the physico-chemical reactions within the system. Thus it is doubtful whether the actual pressure of swelling is identical with the one calculated from the relative vapor pressure. The author reached the same conclusions a few years ago from other considerations.[4] In this connection, C. H. Hill of the department of chemistry of the Massachusetts Institute of Technology, Cambridge, Mass., carried out the following experiment under the supervision of the author:

An air-dried gelatin disc, 3 cm. in diameter and 0.038 cm. thick, was brought into a cylinder of stainless steel whose internal diameter was 3 cm. The lower surface of the sample rested on a porous plate, whose pores were filled with water. The plate was connected with a stand-pipe by means of a small tube. The sample and the porous plate were separated by a thin permeable membrane. A load could be placed on the surface of the sample by means of a piston ground very carefully to fit the cylinder. Although this piston sank into the cylinder under its own weight, the aperture between the cylinder and the piston was almost airtight and entirely watertight.

The air-dried gelatin plate was first of all loaded with 53.2 kg./cm.^{2}, in which case it could take up water through the membrane from the porous plate. The load was then changed in succession to 23.8, 11.5, 5.6, and 23.8 kg./cm.^{2} The changes in the thickness of the plate were measured at regular time intervals with an instrument which permitted direct readings of 1/400 mm. In no case was the pressure changed until the thickness of the plate had remained constant for 24 hours. Consequently, the experiment extended over several months.

In a second series of experiments the concentrations were determined, which corresponded to the relative vapor pressures 0.96, 0.85, 0.73, and 0.31. Four samples were taken for each determination. The initial concentration of two of these was taken higher, and that of two, lower than that which was expected, on the basis of previous experience, to correspond to the vapor pres-

sure in question. The glass containers which held the samples were kept in a water-bath, fitted with an automatic temperature control.

The results of the experiments are shown in Figure 2. The points *a* to *f* show the pressure of swelling measured directly as described above, and the points *g* to *k* the values calculated from the relative vapor pressure. The difference between the two sets of values increases very rapidly with the concentration and is sufficient to give an empirical foundation to the doubts concerning the method used in calculating the pressure of swelling.

In any event it seems evident that the heat of swelling is the product of *two fundamentally different processes.* The one is of a purely physical nature and

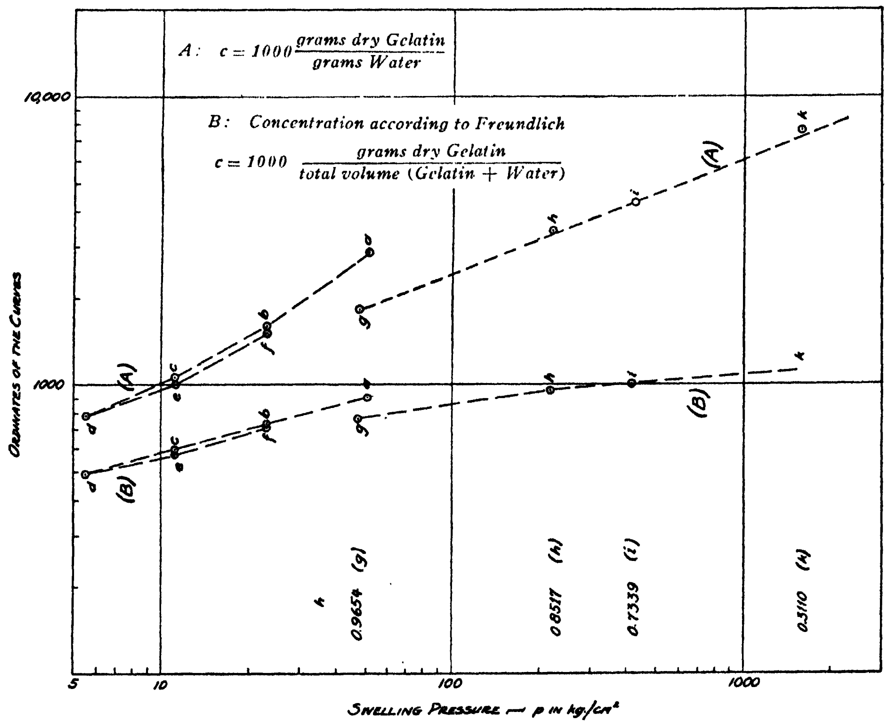


FIG. 2.

arises from the difference between the hydrostatic pressure in the internal and in the external water. The other consists of physico-chemical reactions which take place within the two-phase system. Present views as to the swelling process leave the first of these processes out of consideration. Swelling is considered as due entirely to physico-chemical reactions inside the two-phase system. The swelling pressure is calculated from the relative vapor pressure despite the fact that the formula used has been proved correct only in that case where the lowering of the vapor pressure is due to diminution of the radius of curvature of the menisci. This theory leads to the above-mentioned conclusion that a body in the process of swelling is not under pressure unless the swelling is hindered by mechanical means.

In contrast to this view, the author maintains that the process of swelling merely represents elastic expansion produced by a lowering of the capillary

pressure. According to this point of view, physico-chemical reactions which take place within the systems, influence the swelling only inasmuch as they change the elastic properties of the system by altering adhesion at the points of contact, or stiffness of molecular links or by generating an additional tension in the liquid phase by an osmotic pressure effect. Every two-phase system, capable of swelling, contains a solid phase which is under a pressure equal to the tension in the liquid phase. The presence of this pressure is the essential condition for swelling.

This view on the nature of swelling is strongly supported by the remarkable correlation which exists between the swelling of coarse and of fine disperse systems, caused by a reduction of the external pressure under which these systems stand. The following paragraphs will show this correlation more clearly.

Volume-Elasticity of Sand-Mica Mixtures and of Clays.

If pressure is exerted on sand which cannot expand laterally, it will become more closely packed. The removal of the pressure causes an elastic expansion. The relation of pressure to the voids ratio of various sands is

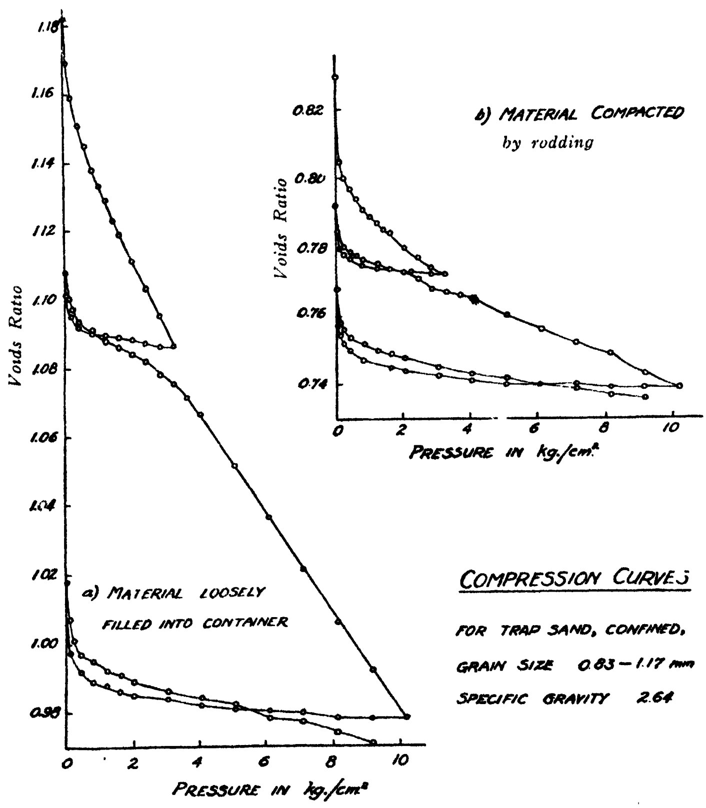


Fig. 3.

shown in Figure 3. The voids ratio is the quotient of the volume of the pores divided by the volume of the solid particles. The shape of the descending

curve (compression curve) in Figure 3 is largely dependent on whether the initial packing of the material was loose or tight, whereas the ascending branch (swelling curve) corresponding to the lowering of pressure is scarcely influenced by the initial state.

The relation between the external pressure and the voids ratio in plastic clays was determined by the extensometer shown in Figure 4. The sample was placed between two porous plates of "Alundum" (S) with an average pore diameter of 0.09 mm. The upper plate is built into the bottom of a piston p (diameter 7 cm.) which is ground to fit the cylinder C. The pores of the lower plate communicate with two small glass stand-pipes (H). Discs of thin filter

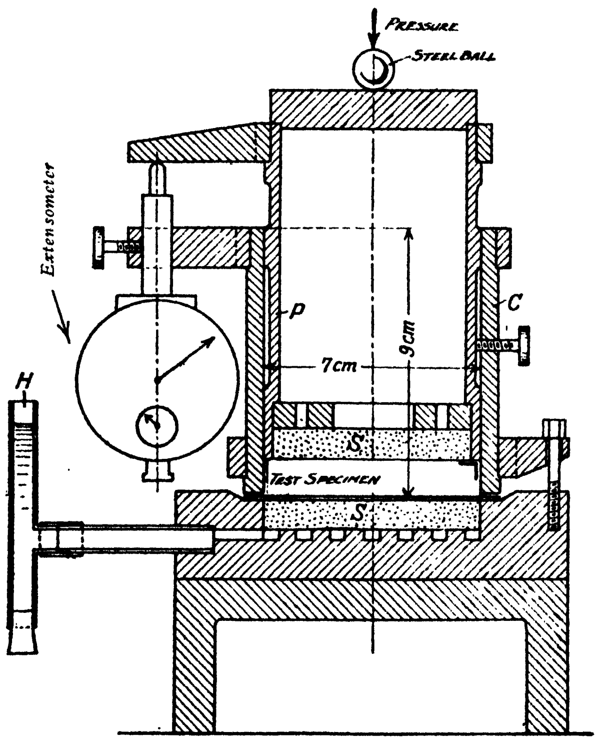


Fig. 4.

paper prevent soil particles from entering the pores of the porous plates or getting between piston and cylinder. Pressure is applied either with a simple lever arrangement or, for higher pressure, with an oil-pressure testing machine. The readings are taken with an Ames dial (direct reading 1/400 mm.). During the experiment the water level in the stand-pipes is kept about 2 cm. higher than the sample. In the case of a plastic clay in a layer 1.5 cm. thick, the difference in hydrostatic pressure produced by changes in pressure persist for about 12 hours so that two points on the pressure/voids ratio curve may be determined daily. Figure 5 shows some typical pressure/voids ratio curves for "lean" and "fat" clays. The steep descending curve represents compression and the flat ascending one is the swelling curve.

The only difference between water-saturated clays (Fig. 5) and dry sand (Fig. 3) is that both swelling and compression are more pronounced with the clays. For both materials the swelling curve follows for all practical purposes the formula:

$$\frac{dp}{d\epsilon} = -A\,(p + p_1) \doteq -Ap. \qquad (1)$$

where p is the pressure per unit area, ε the voids ratio and A a constant, which later on will be called the elasticity factor.[5] The reciprocal value of the elasticity factor may be called the swelling index. The form of the swell-

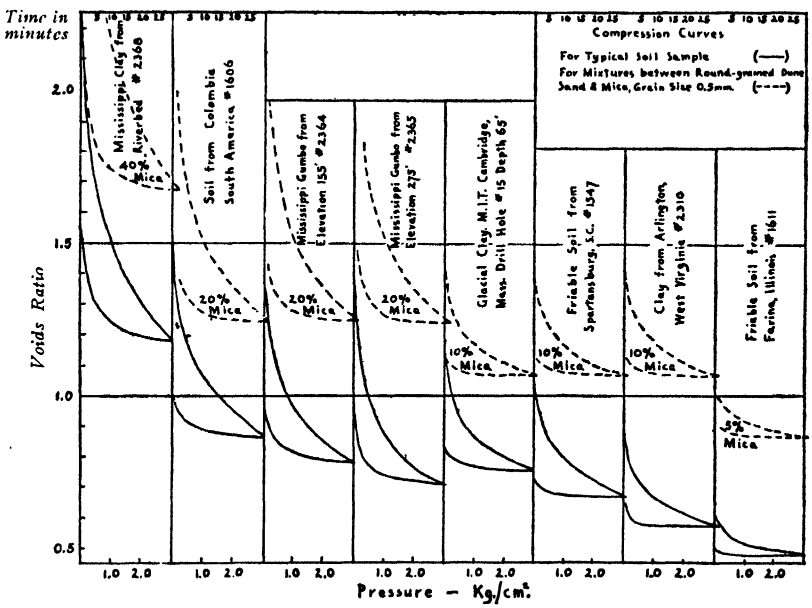


FIG. 5.

ing curve and the extent of the swelling is determined by the value of A. The bigger this value, the *less* swelling takes place when the pressure is reduced. The value of A varies for soil samples from about 260 for sands to 8 for very fat clays.

It was suspected that the high swelling capacity of clays was due to a large percentage of scaly mineral matter. To test this assumption the voids ratio diagrams of coarse-grained sand-mica mixtures with varying amounts of mica were obtained. These experiments were carried out in 1927 by G. Gilboy under direction of the author.[6] It was shown that coarse mixtures made with an appropriate content of mica had swelling capacities identical with those of fat water-saturated clays, both quantitatively and qualitatively. The pressure/voids ratio diagrams of these "equivalent" sand-mica mixtures are shown in Figure 5 with broken lines. Figure 6 gives the relation between the percentage of mica and the elasticity factor for coarse-grained mixtures. There remained a possibility that this agreement between the pressure-voids ratio of fat clays and coarse mixtures was accidental. This possibility was disproved,

at least for Norwegian clays, by the investigations of V. M. Goldschmidt, who showed by optical and chemical means that the composition of Norwegian clays is as follows: Scaly mineral constituents (chlorite, talc, muscovite, biotite), 12.0 to 27 per cent; needle-like mineral constituents (hornblende, epidote, etc.), 4.5 to 13.8 per cent; equidimensional mineral constituents (feldspar, quartz, apatite, ilmenite, rutile, limonite), 60.7 to 72 per cent.

The maximal amount of scaly mineral constituents of Norwegian clays agrees remarkably well with the amount of mica which must be added to sand in order to produce a mixture whose swelling capacity is similar to that of fat clay.

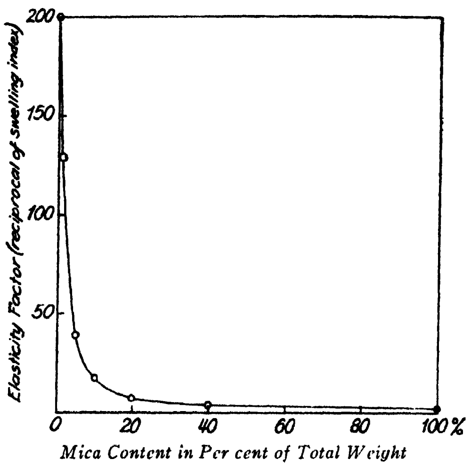
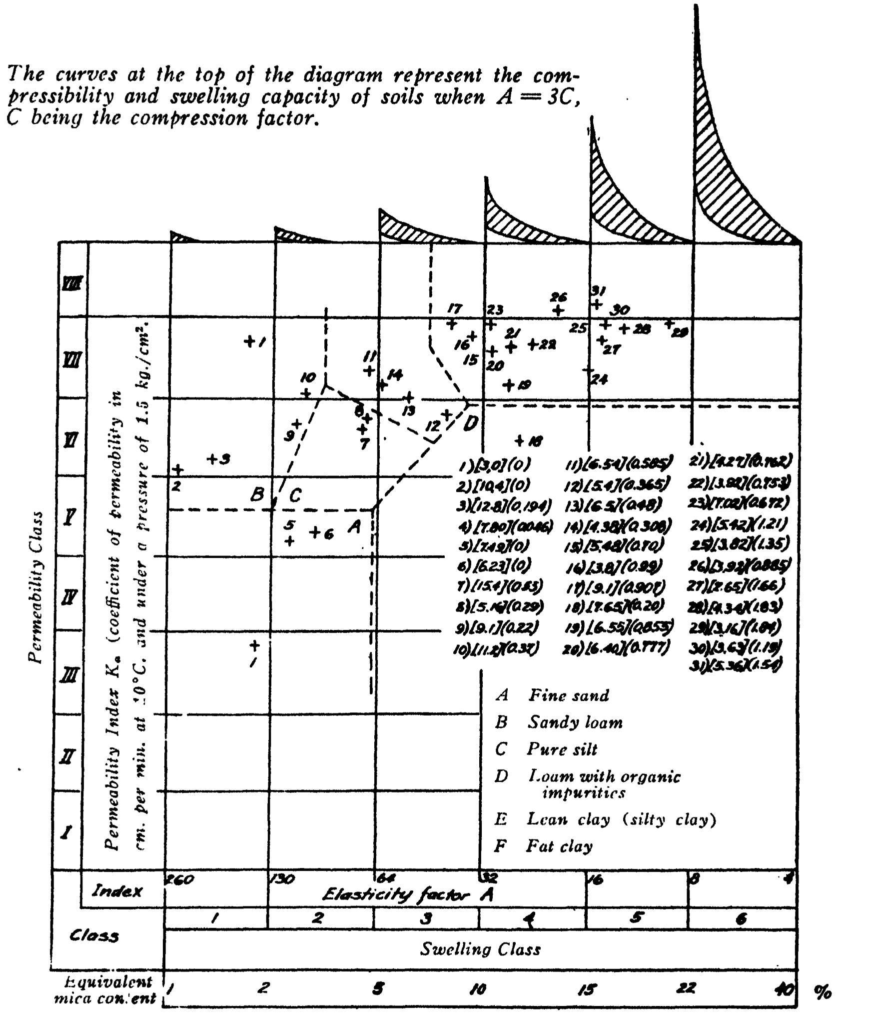


FIG. 6.

Figure 7 gives a summary of porosity and swelling capacity of the more important soil types. The ratio $\frac{A}{C}$ (elasticity factor divided by the compression factor) and the plasticity index (as defined by Atterberg, but expressed in terms of the voids ratio) are on the list accompanying the diagram. Above each column was plotted the compression curve and the swelling curve for the soil represented by the column on the assumption that the value of $\frac{A}{C}$ equals 3. It can be seen from this diagram how quickly the compressibility and swelling capacity of soils increase as one proceeds from fine sands (left) to fat clays (right).

The data given show that the degree of dispersion has little to do with swelling capacity in fat clays. Since the swelling capacity of coarse disperse members of this group is entirely dependent on the elasticity of the particles and particle-groups, one is justified in assuming that the swelling capacity of fine disperse two-phase systems is dependent on the elastic properties of the solid phase. The physico-chemical reactions between the solid and the liquid phase (formation of adsorption compounds within the system) can at best only play a minor rôle.



Figures within [ ] are the ratio of the elasticity and compression factor.

Figures within the ( ) are the plasticity index according to Atterberg, expressed in terms of the voids ratio.

Fig. 7.

True and Apparent Cohesion of Clays.

When the concentration of a thick clay slurry is increased by consolidation under pressure, the material becomes coherent, that is, acquires compressive, tensile and shearing strength. Figure 8 shows the result of a compression test on a stiff plastic cylindrical sample of material laterally unsupported. The horizontal axis gives the pressure per unit area and the vertical axis, i.e. the corresponding compression. The main branch *OA* of the pressure curves is approximately parabolic, while the hysteresis loops *cd*, *ef*, are practically straight lines. If the pressure is kept constant, say at "*a*," the degree of consolidation

increases, but at a diminishing rate, and approaches asymptotically the value given by the point "b." This phenomenon corresponds to the elastic after-effect of solid bodies.* Owing to the complete agreement between the pressure diagrams of stiff plastic clay and granular solids (rock or concrete) the usual terms of applied mechanics can be used to express results. Applying in the customary fashion the term modulus of elasticity (pressure divided by the corresponding compression) to the reversible deformation of the sample, the modulus of elasticity can be considered constant for each clay cube, because the hysteresis loops are parallel at moderate pressures. Its value E is given by the cotangent of the angle α which is formed by the hysteresis loop and the axis of abscissas. Figure 9 shows the results of compression tests on four clay cubes, which contain the same solid phase but different water content, the voids ratio ε having the values 0.792, 0.681, 0.490, and 0.482 respectively. Below each diagram are plotted the changes that take place over a period of time, while external conditions remain constant.

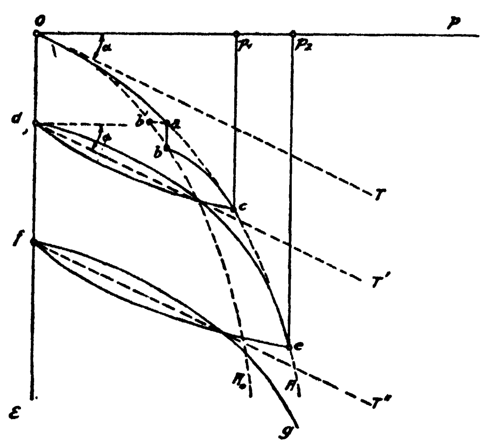


FIG. 8.

The enormous influence of concentration on the modulus of elasticity and on the crushing strength made it interesting to study the influence of the previous history of the sample on its elastic properties. Dr. Joseph Janiczek of Budapest carried out the following experiments along this line at the Soil Mechanics Laboratory of the Massachusetts Institute of Technology in Cambridge, Mass., under the direction of the author.

A considerable quantity of the clay soil to be examined was thoroughly mixed with water to form a soft plastic mass. This was divided into a number of equal parts, which underwent a series of changes of condition as shown in Figure 10a. The extensometer shown in Figure 4 was used.

In order to produce the conditions a, e, or i, the extensometer was filled with the soft plastic clay sample and the stand-pipes H (Fig. 4) filled with water. Then the pressure acting on the sample was increased gradually to p_1, p_2, and p_3, respectively, and held constant until the extensometer registered no further compression. At this point, the stand-pipes H were emptied, the hood removed and the sample taken out before it had time to swell. Finally circular plates of 2.5 cm. diameter were punched out of each sample and these were placed

* In a similar way, at a constant voids ratio ε, the swelling pressure p decreases in time and approaches asymptotically the value given by the absicssa of the point b in Fig. 8.

one on top of the other until a cylinder 2.5 cm. high was obtained. This cylinder, carefully prevented from drying out, was used for compression tests as shown in Figures 8 and 9. Under the stated conditions, it was admissible to assume that as soon as the pressures, p_1, p_2, and p_3, respectively, were removed, they were replaced by the surface tension of the water (capillary pressure) as shown in Figure 1b.

To produce the conditions *d, h* and *m* the clay sample was brought to equilibrium under the pressures, p_1, p_2, and p_3 respectively. The pressure was then reduced gradually to zero and the sample left in the extensometer until measurements indicated that the swelling process was completed.

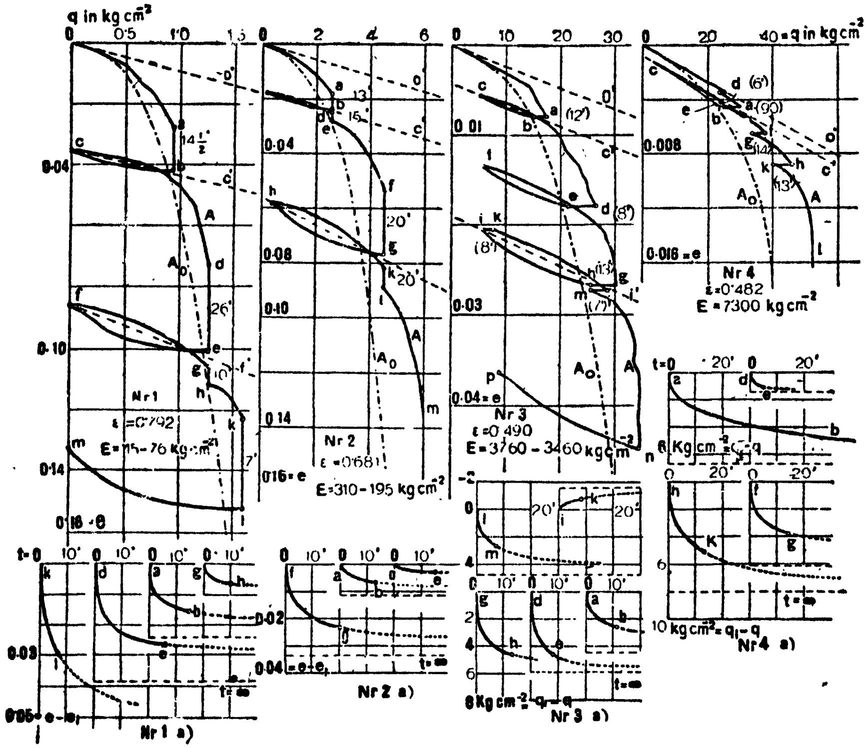


FIG. 9.

The results of the experiments are shown schematically in Figure 10b. The modulus of elasticity and the compressive strength increase almost in direct proportion to p in those conditions represented by the main curve o i (curves E and $q_{d\,max}$). This fact was recognized by the author some years ago.[8] Under the conditions *d, h,* and *m,* the modulus of elasticity appears to increase in direct proportion to that pressure p'_1, p'_2 or p'_3, respectively, which is necessary to lower the voids ratio from its initial value to those indicated by the points d', h' and m' on the main curve.

The rectilinear course of the lines E and $q_{d\,max}$ are readily comprehensible. Each sample, corresponding to a point on the graph, stands, during the experiment, under the influence of a capillary pressure whose value is given by the abscissa p of the point. The capillary pressure produces internal friction equal

to the product of capillary pressure and the coefficient of internal friction. The internal friction so produced is therefore directly proportional to the capillary pressure. The relation between internal friction, compressive strength and modulus of elasticity is also constant. Therefore the lines E and $q_{d\,\max}$ must be straight. Since the cohesion of the samples corresponding to the lines E and $q_{d\,\max}$ is mainly due to the capillary pressure caused by the surface tension of the water, it can be called "apparent cohesion."

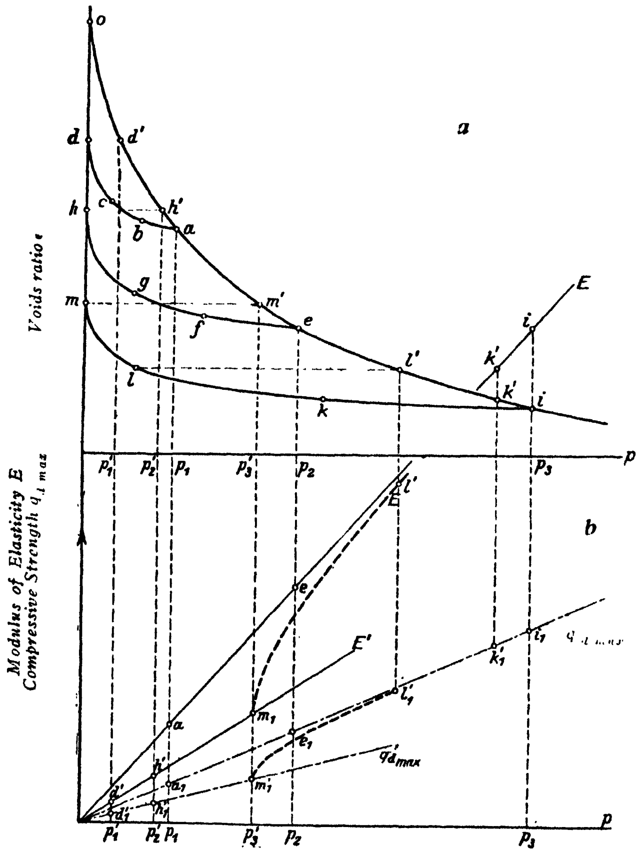


FIG. 10.

For the samples corresponding to the lines E' and $q'_{d\,\max}$ the capillary pressure is equal to zero (Fig. 10a). The cohesion of the samples can be accounted for only by molecular bond between the particles and must therefore be called "true cohesion." The rectilinear course of the lines $q_{d\,\max}$ and $q'_{d\,\max}$ seems to show the following: Internal frictional resistance in a two-phase system caused by increase of pressure increases in direct proportion to the pressure, as does ordinary frictional resistance. While, however, in coarse disperse systems the frictional resistance decreases almost proportionately to the decrease in pressure, in fine disperse and imperfectly elastic two-phase systems, part of the frictional resistance, when once evoked, is not reversible. If the pressure

is completely removed from the system, the irreversible part (true shearing strength) amounts to a definite percentage of that frictional resistance, which, with the same voids ratio, would correspond to the total capillary pressure. Let us assume that the voids ratio of a two-phase system has been decreased to ε_1 by exerting a pressure p per unit of surface. The corresponding resistance due to internal friction amounts to fp_1, where f is the coefficient of internal friction. By further increasing the pressure and subsequently releasing it, we may change the condition of our system so that the voids ratio is again ε_1, although the system is under no external pressure. In this case the shearing strength of the system is nfp_1, where $n < 1$ is a coefficient characteristic of the given system and independent of p_1. The value of n seems to increase with increasing dispersion.

The voids ratio, like the water content of a two-phase system, is a direct measure of the concentration. According to what precedes, the clays represent colloid-rich two-phase systems which, at the same concentration, can either swell very vigorously or not at all, depending on the mechanical procedure used to reach this concentration. Since the concentration is a direct measure of the physico-chemical energy of the system, it is evident for such systems that the swelling pressure is solely dependent on the intensity of the purely physical capillary pressure, which is equal to the tensile stress in the interstitial water.

The Time Factor in the Swelling of Coarse Disperse Two-Phase Systems.

If pressure is exerted on a coarse disperse two-phase system which is covered with a filter plate, consolidation occurs and the excess water escapes through the filter plate. The time rate at which the water leaves the system depends on the permeability of the system. The influence of permeability on the speed with which the volume changes is demonstrated by the model in Figure 11, which shows a compression cylinder with a perforated piston that rests on spiral springs. The space below the piston is filled with water. When the pressure on the piston is increased, the piston can sink only as quickly as the water underneath it can get away. The smaller the openings,

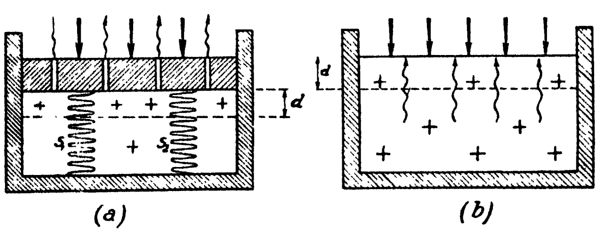


Fig. 11.

the slower the piston sinks. The difference between the case shown in Figure 11b and that of Figure 11a is, that in the case of Figure 11b, the water escapes through the coarse disperse two-phase system whose intercommunicating interstices permeate the whole mass. Figure 12 shows the relationship between time (horizontal axis) and compression (vertical axis) for three soil types with very different coefficients of permeability. The experiments were carried out with the aid of the extensometer (Fig. 4), and in all three cases the pressure was raised in a few seconds from 1.6 kg./cm.^{2} to 3.1 kg./cm.^{2} The figure "100 per cent" relates to the consolidation after 17 hours. The slight

retardation of consolidation of the most permeable soil sample (Fig. 12a) is due entirely to the gradual equalization of the uncompensated frictional resistance, and has nothing to do with the resistance to flow. This retardation is not so noticeable in the other two systems, as it is small in comparison to retarda-

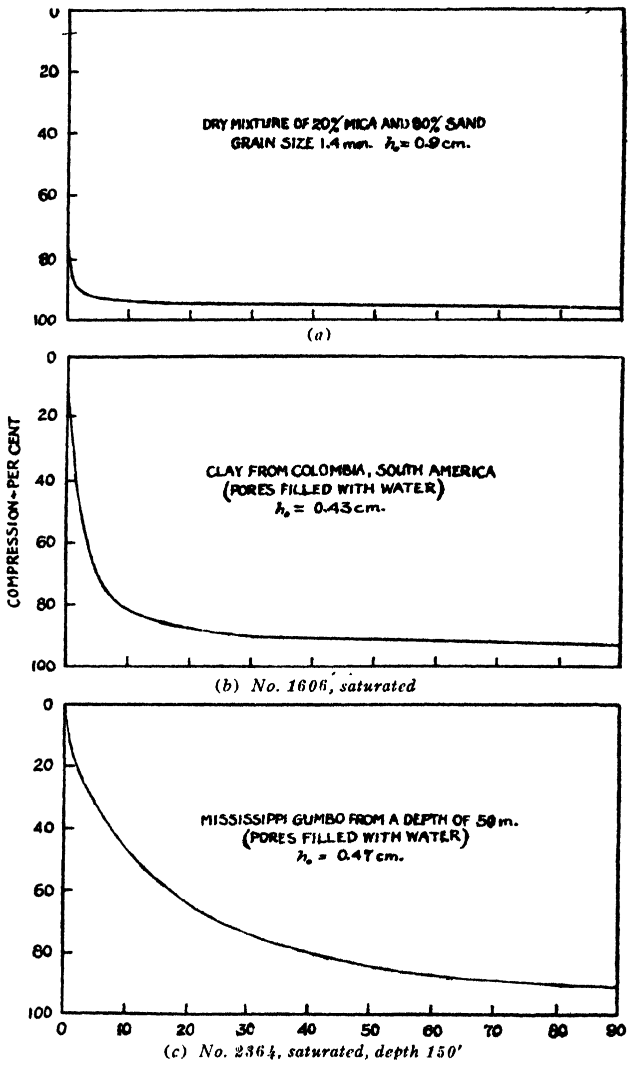


FIG. 12.

tion due to low permeability. In contrast to retardation due to the gradual equalization of frictional stresses, that due to low permeability is proportional to the square of the thickness of the compressed layer. Before reaching a final value, part of the load acting on the sample is taken up by the hydrostatic pressure in the interstitial water.

The author has analyzed [9] the relations between time, permeability, and elastic constants of a two-phase system on the basis of the following assumptions:

That the law of Darcy, stating that the rate of flow is proportional to the hydraulic gradient, is valid;

That the coefficient of permeability and the coefficient of consolidation (*vide infra*) may be considered constant for the concentration interval, over which the process extends.

Let h be the thickness of a layer of a two-phase system under the pressure p_0. The system is covered with a filter plate and cannot expand laterally. The underlying plate is non-porous.

p_0, the pressure per unit area (grams per cm.^{2}), acting on the layer before the experiment begins,

$p_0 + p_1$, the pressure per unit area to which the pressure is raised the moment the experiment starts,

t, the time in minutes elapsed since the moment when the pressure was suddenly raised, at the beginning of the experiment, from p_0 to $p_0 + p_1$,

ϵ_0, the voids ratio at the beginning of the experiment,

ϵ, the voids ratio at the time t,

ϵ_1, the voids ratio at the time $t =$ infinity,

$\Delta\epsilon = \epsilon_0 - \epsilon$, the calculated consolidation after the time t,

$\Delta\epsilon_1 = \epsilon_0 - \epsilon_1$, the calculated consolidation after the time $t =$ infinity,

$a = \frac{\Delta\epsilon_1}{p_1}$, ($p_1$ in gram per cm.^{2}), the coefficient of compressibility, i.e. the decrease of the voids ratio for an increase in pressure of 1 gram per cm.^{2},

k, the coefficient of the permeability in cm. per minute, i.e. the time-ratio with which the water leaves the two-phase system at a hydraulic gradient $i = 1$,

$v = \frac{k}{a(1 + \epsilon_0 + \frac{1}{2}\Delta\epsilon_1)}$, the coefficient of consolidation for the pressure interval p_0 to $p_0 + p_1$, or for the voids ratio interval ϵ_0 to ϵ_1.

Then the following result was obtained by the application of the laws of hydraulics to the process of consolidation.[9]

$$\Delta\epsilon = \Delta\epsilon_1 \left[1 - \frac{8}{\pi^2} e^{-\frac{v\pi^2(1+\epsilon_0)^2}{4h^2}t} - \frac{8}{9\pi^2} e^{\frac{-9v\pi^2(1+\epsilon_0)}{4h^2}t} - \cdots\cdots \right.$$
$$\left. \cdots\cdots - \frac{8}{(2n+1)^2\pi^2} e^{\frac{-(2n+1)^2 v\pi^2(1+\epsilon_0)^2}{4h^2}t} \right] \qquad (2)$$

Figure 13 shows the relation between time and compression according to Formula (2) on the basis of the assumptions that: $\Delta\varepsilon_1 = 100$, and $\frac{v\pi^2(1+\varepsilon_0)^2}{4h^2} = 1$.

To determine the coefficient of consolidation v from an empirically determined time-consolidation curve, the following method was suggested.[10] The quotient t_1 divided by t_2 is calculated for various values of $\Delta\varepsilon$ where t_1 is the time necessary for the compression to reach the value $\Delta\varepsilon$ and t_2 the time for the voids ratio to reach half that value, or $\frac{\Delta\varepsilon}{2}$. If the values of $\Delta\varepsilon$ are taken as ordinates and those of $\frac{t_1}{t_2}$ as the corresponding abscissas, a hyperbolic

curve is obtained. In Figure 13 this curve is shown by a dashed line. On this curve the point P', having an abscissa $\frac{t_1}{t_2} = 5.27$, is located. The theory of this method gives for the coefficient of permeability k of a two-phase system the formula below:

$$k = 0.85 \frac{h^2\left(1 + \epsilon_0 + \frac{\Delta\epsilon_1}{2}\right)}{(1+\epsilon_0)^2 t_1} a \tag{3}$$

or with sufficient accuracy

$$k = 0.85 \frac{h^2 a}{(1+\epsilon_0) t_1} \tag{3a}$$

where t_1 is the time in minutes corresponding to the point P. The values for a and ε_0 are to be taken from the curve representing the relation between the pressure p and the voids ratio ε. Figure 14 gives the results of a series of experiments carried out with a fat clay from the Mississippi valley. The full curves in the time voids ratio diagrams (Fig. 14B to E) show the empirical data and the dashed lines are the theoretical curves obtained from Formula 2. The differences between the empirical and the calculated values is considerable

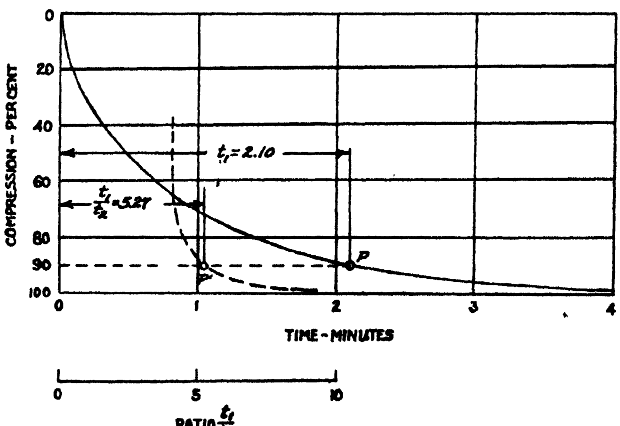


FIG. 13.

only for large values of t_1 because here the course of the consolidation is markedly influenced by uncompensated frictional stresses (*see* Fig. 12a and the text) which have not been considered in Formula 2. However, since the graphical methods for determining the values k and v makes use only of the steeper part of the curve, which is little influenced by frictional stresses, the values for the coefficient of permeability calculated from the empirical data by means of Formula 3 agree quite well with values obtained from direct permeability experiments.

Experiments carried out with various samples of loam and clay lead to the following conclusion:

The coefficient of permeability of clays decreases very rapidly with decreasing voids ratio i.e. with increasing concentration. The experimental data of Fig. 14 are a good example of this decrease.

The viscosity of water increases very rapidly with a decrease of the diameter of very narrow capillaries.[11] The following empirical relationship was deduced from the results of the experiments:

$$\eta = \eta_0\left(1 + \frac{\alpha \times 10^{-42}}{d^3}\right), \tag{4}$$

where n_0 is the normal viscosity of water (in cgs. notation) at a temperature T,
n, the viscosity of water in a narrow slit at the same temperature,
d, half the width of the slit in cm.,
α, a constant, the value of which probably lies between 6.0 and 0.24.

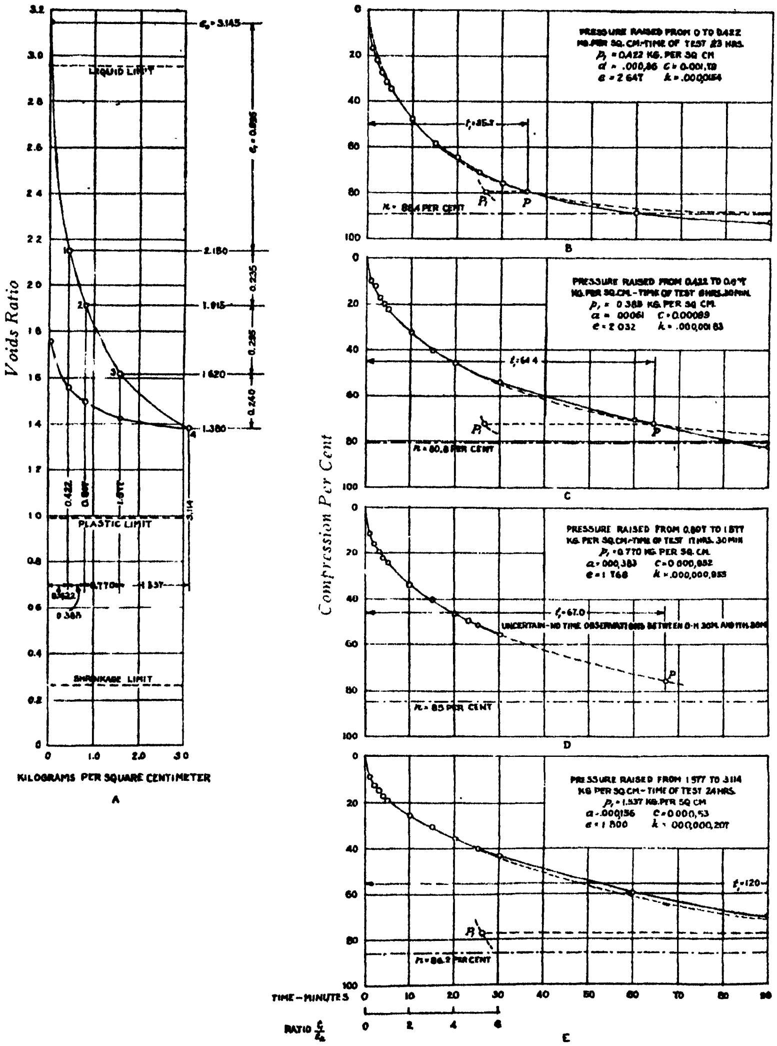


FIG. 14.

INELASTIC AND ELASTIC GELS.

The term inelastic gel is incorrect inasmuch as inelastic gels cannot exist. Even silica gel must possess a certain elasticity; but like the elasticity of sand, it is only perceptible when the most delicate measuring instruments are used. The elastic properties of inelastic gels coincide presumably in every way

qualitatively with those of very strongly swelling clays (*see* Fig. 5). One should, therefore, divide gels in the same way as solid bodies into imperfectly elastic and perfectly elastic gels. Each of the two groups would contain transition stages between slightly and highly elastic gels. Imperfectly elastic gels, composed of separate particles, have very different degrees of elasticity, as shown in Figures 5 and 7. The question then arises as to whether the elasticity of such systems is directly due to the elastic deformation of the component particles, or whether it may also be in part due to the reversible displacement of the particles relative to one another. Calculations carried out for quartz sand show that the first factor, deformation of the particle, is small in comparison to the second.[12] The relative displacement of particles can, however, not possibly be completely reversible, since every particle tends to move towards a more stable position. It is, therefore, justifiable to assume that disperse systems built up of separate particles *must* be imperfectly elastic. Almost perfectly elastic gels (gelatin, rubber, etc.) experience, under pressure, volume changes that are almost completely reversible. Therefore, such systems cannot consist of particles, independent of each other. The particles must be bound together and form a sponge-like network, so that in the event of a deformation (volume contraction or expansion) there is no sliding between the individual particles of the system.

Time-Rate of Swelling of Gelatin.

Valuable studies on the time rate of swelling of gelatin have been suggested by H. Freundlich and carried out by E. Posnjak on circular gelatin plates with a thickness of 0.3 mm., using the Reinke [13] extensometer. From the results it appeared that the velocity of swelling represents a reaction of the first order.

Let w be the water content of a gel at a time t after the beginning of the experiment; and w_∞, the water content at the time $t =$ infinity, that is, after the equilibrium has been reached, and by Λ an empirical constant. Then

$$\frac{1}{t} \ln \frac{w_\infty}{w_\infty - w} = \Lambda,$$

and from that

$$\frac{w_\infty}{w_\infty - w} = e^{\Lambda t} \qquad (5)$$

The value of Λ was found to be almost independent of the concentration. The swelling process could, however, also be a purely hydro-mechanical phenomenon. This may be seen from the following considerations: The relation between time and the average water content for such a process is given by formula (2). From this formula may be determined the extent to which the swelling process described by formula (5) coincides with the theoretical course of the hydro-mechanical swelling process (soaking up of water due to the elastic expansion of a permeable body). The voids ratio ε in formula (2) gives the volume of the voids per unit of volume of the dry substance. Therefore the change Δw of the water content in per cent of the dry weight due to the change of the swelling pressure is

$$\Delta w = \frac{\Delta \varepsilon}{\gamma}$$

where γ is the specific gravity of the dry substance. After a time, $t =$ infinity, the values of $\Delta\varepsilon$ and Δw reach $\Delta\varepsilon_\infty$ and Δw_∞ respectively. The value of Δw_∞ is given by the formula

$$\Delta w_\infty = \frac{\Delta\epsilon_\infty}{\gamma} = \frac{a.p_1.h}{\gamma(1+\epsilon)}$$

If we substitute the values Δw and Δw_∞ into the formula (2), we obtain:

$$\Delta w = \frac{\Delta\epsilon}{\gamma} = \Delta w_\infty \left[1 - \frac{8}{\pi^2} e^{-\frac{v\pi^2(1+\epsilon_0)^2}{4h^2}t} - \frac{8}{9\pi^2} e^{-\frac{9v\pi^2(1+\epsilon_0)^2}{4h^2}t} \cdots\cdots \right.$$
$$\left. \cdots\cdots - \frac{8}{(2n+1)^2\pi^2} e^{-\frac{(2n+1)v\pi^2(1+\epsilon_0)^2}{4h^2}t}\right] \quad (6)$$

For small values of h the series converges very rapidly, so that we can neglect all the members of the series after the second. On this assumption the formula (6) becomes

$$\Delta w = \Delta w_\infty\left[1 - \frac{8}{\pi^2} e^{-\frac{v\pi^2(1+\epsilon_0)^2}{4h^2}t}\right] = \Delta w_\infty\left[1 - 0.81\, e^{-\frac{v\pi^2(1+\epsilon_0)^2}{4h^2}t}\right] \quad (7)$$

from which follows

$$e^{\frac{v\pi^2(1+\epsilon_0)^2}{4h^2}t} = e^{\Lambda t} = 0.81\,\frac{\Delta w_\infty}{\Delta w_\infty - \Delta w} \quad (8)$$

where

$$\Lambda = \frac{v\pi^2(1+\epsilon_0)^2}{4h^2} \quad (8a)$$

Formula (8) differs from the Posnjak formula (5) only by the presence of the factor 0.81, which can be partially explained by the omission of the members of higher order.

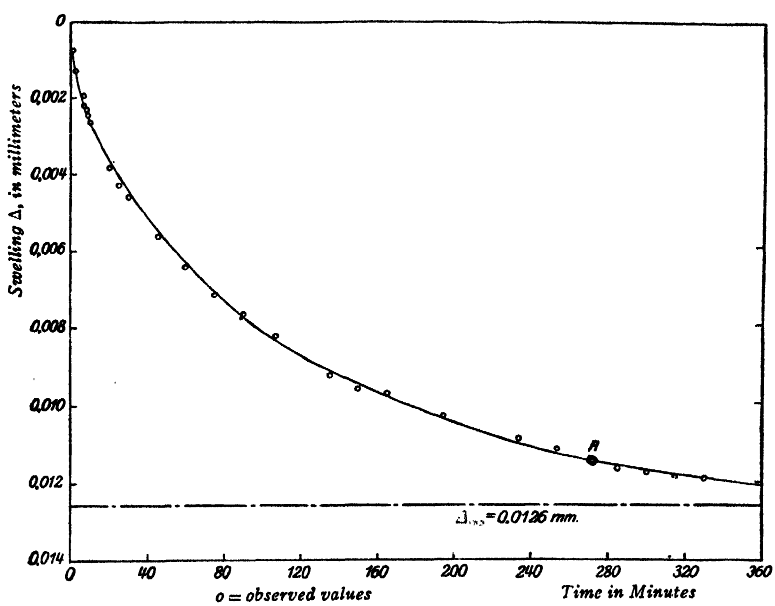


FIG. 15.

As already mentioned, the experiments of Hill on the time rate of swelling and consolidation of gelatin were carried out with great accuracy (direct reading 1/400 mm.). The points indicated in Figure 15 by small circles give

the observed results of the amounts of swelling, A, of the specimen which took place when the pressure was reduced from 11.57 to 5.68 kg./cm.^{2} In order to see how far the actual process conforms with formula (2), a curve based on this formula was drawn through the point A, chosen at random. This formula, represented by a full line in the diagram, agrees in a remarkable manner with the observed results for gelatin, and much better than for the coarse disperse and permeable two-phase systems for which the equation was derived.

It is further remarkable that the deviations between calculated and observed results are alternatively positive and negative. Similar alternating deviations were observed without exception in coarse disperse two-phase systems, and seem to be the result of the gradual accumulation and subsequent release of frictional stresses.

Coefficient of Permeability and the Structure of Gelatin.

The time-rate of the consolidation process under constant pressure has been for many years used by the author to determine experimentally the coefficient of permeability of clays and other feebly permeable two-phase systems. Using the above mentioned semigraphical method, the results of Hill's experiments with isoelectric gelatin gave the following values for the coefficient of permeability:

Pressure in kg./cm.^{2}	Voids Ratio ε	Coefficient of Consolidation v	Coefficient of Permeability k in cm./min.
53.09 — 23.92	0.46 — 0.83	$1.27 \cdot 10^{-5}$	$1.06 \cdot 10^{-10}$
23.92 — 11.57	0.83 — 1.25	$3.42 \cdot 10^{-5}$	$2.80 \cdot 10^{-10}$
11.57 — 5.68	1.25 — 1.72	$8.00 \cdot 10^{-5}$	$5.07 \cdot 10^{-10}$

Figure 16 shows the relation between the load p in kg/cm.^{2} and the voids ratio ε for a fat, yellow clay (Curve C_1), and for gelatin according to the results of Hill (Curve C_2). The arrows indicate the direction of the pressure variations. The curves K_1 and K_2 on the same diagram show the relation between the voids ratio ε and the coefficient of permeability k of the fat clay (K_1) and for the gelatin (K_2). The main difference between the graphs C_1 and C_2 lies in the disparity between the total and the reversible concentration changes, which are greater for clay than for gelatin. The character of the curves is however very similar, a fact which has been mentioned elsewhere.[14]

Of far greater importance is the difference between the curves K_1 and K_2. The permeability of the clay decreases very rapidly with decreasing voids ratio (i.e. increasing concentration), while under the same circumstance the permeability of gelatin decreases slowly. This obvious difference can be explained only by assuming that the size of the interstitial capillary spaces of gelatin is less affected by the decrease in the voids ratio, than is that of clay. Two systems of approximately similar structure could not show the fundamental difference illustrated by the curves K_1 and K_2. The course of curve K_2 reveals a system which, in contra-distinction to clay, has a spongy or skeleton structure, an assumption which harmonizes very well with the elastic behavior of the substance.

Further data on the structure of gelatin have been obtained from the evaluation of the size of the openings through which the water flows. According to Figure 16 the value of the coefficient of permeability k for gelatin

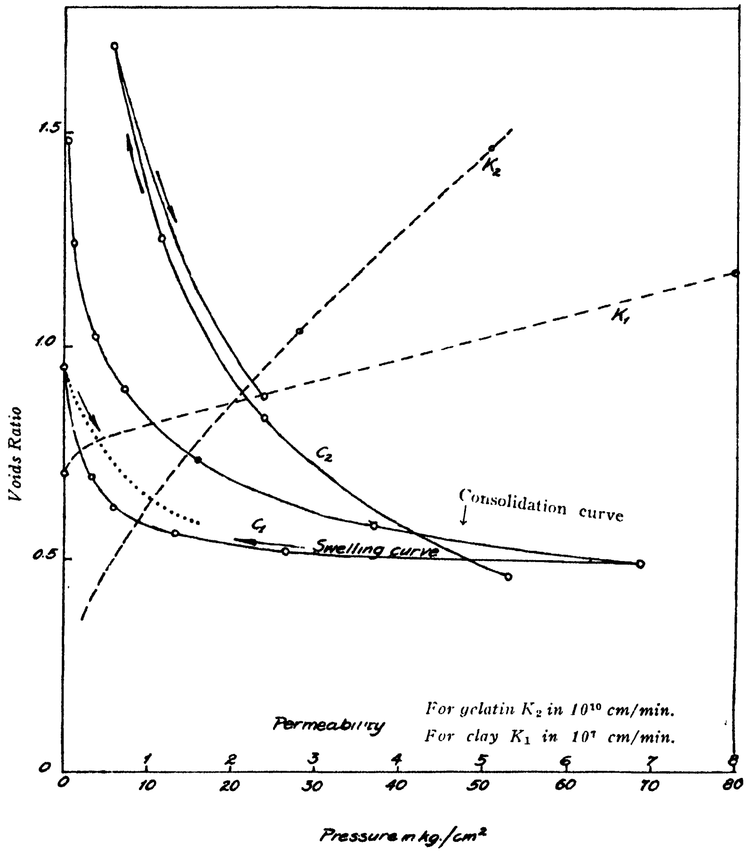


FIG. 16.

is 2.6×10^{-10} cm. per minute, when the voids ratio $\varepsilon = 1$. Let us assume that gelatin is composed of particles like sand with a diameter d, measured in centimeters, that the water flows through channels of variable diameter, and that, furthermore, the viscosity of the water is normal. The author has deduced for this type of permeable system the following approximate formula, which is mentioned elsewhere: [15]

$$k \text{ (cm. per minute)} = 60.63 \frac{\eta_0}{\eta_t} \frac{n - 0.13}{\sqrt[3]{1-n}} . d^2 \text{ (cm.)}, \qquad (9)$$

where $n = \dfrac{\varepsilon}{1+\varepsilon}$ is the pore volume (in our case $\varepsilon = 1$ and $n = 0.5$), and η_0 and η_t represent the viscosity of water at 10° or at $T°$, respectively, the latter being the temperature at which the experiment is carried out. If we introduce into formula (9) a value for k of 2.6×10^{-10} cm. per minute, and for the temperature T the value 20° C., we obtain

$$d = 1.57 \times 10^{-7} \text{ cm.} = 1.57\ m\mu$$

The diameter of the particles between which the water flows cannot possibly be so small. However the experiments on clays have led to the conclusion that the viscosity of water in very narrow flow-sections is considera-

bly greater than the viscosity of free water [*see* note to formula (4)]. Formula (9) is therefore not applicable to finely disperse systems.

A further calculation was carried out, assuming that the viscosity of water conforms to formula 4, and that the water passages through the gel consisted of slits with impermeable walls running parallel to the direction of the flow, and with a width d. The total volume of the slits (ε being 1) is assumed to be half the volume of the permeable system. The coefficient of permeability k can then be expressed as follows:

$$k = 2.6 \times 10^{-10} \text{ cm. per min.} = \frac{d^2}{24\eta\left[1 + \frac{\alpha \times 10^{-42}}{\left(\frac{d}{2}\right)^8}\right]}$$

where η is the viscosity of the free water in c.g.s. at the temperature of the experiment; d, the width of the slits in centimeters; α, a constant, having a value between 6.0 and 0.24. Solving for d, we obtain the value 4.2×10^{-6} to 3.0×10^{-6} cm., or $d = 42\ m\mu$ to $30\ m\mu$ with a mean value of $36\ m\mu$. This value is apparently somewhat too large. In order to obtain a value more in harmony with the existing ideas on the size of gelatin molecules, one would have to assume that the water does not flow through tube or slit-shaped channels but through the web of a spacial network.

Three different groups of facts lead, therefore, to the assumption that gelatin has a sponge or net-like structure: (1) the almost perfect elasticity which precludes on mechanical grounds the idea that gelatin is composed of individual grains (2) the abnormal shape of the curve K_2 in Figure 16; and (3) the results of the evaluation of the size of the openings on the basis given above.

The influence of the solid phase on the viscosity of the interstitial water which is notable even in the case of clays, is doubtless a very important factor in producing the viscosity of gelatin containing much water. The average viscosity of water in gelatin with a spongy structure, would be considerably greater than that of water contained in a system of slits with a calculated average width $d = 36\ m\mu$.

By introducing the values for d in the formula (4), the average viscosity of water in a slit system is found to be between 16,000 η and 10,000 η, or in other words approximately 13,000 times greater than the viscosity of free water. The average viscosity of the pore water of a gelatin sample with a voids ratio $\varepsilon = 1$ is probably considerably higher.

The value Δ in formula (8a) can be used to estimate roughly the coefficient of permeability of a gel of a given concentration c and also to gage the influence of dissolved substances on the permeability, provided we know the change in concentration Δc which is caused by a change in pressure of 1 g./cm.[2]

The relation between the voids ratio ε (volume of the interstitial spaces per unit volume of the dried substance) and the concentration c as defined by Freundlich (grams of dried substance per 1,000 cc. of the total volume of the gel, as follows:

$$c = \frac{1{,}000\,\gamma}{1 + \varepsilon} \tag{10}$$

where γ is the specific gravity of the dried substance. This formula makes it possible to calculate from the initial concentration c_0 either of the following: (1) the *initial* voids ratio associated with a change in concentration due to a

change in pressure; (2) the *change in* voids ratio associated with a change in pressure.

From the equation (8a) we get:

$$\Lambda = \frac{v\pi^2}{4h^2}(1+\epsilon_0)^2 = \frac{k\pi^2(1+\epsilon_0)^2}{4ah^2(1+\epsilon_0+\frac{1}{2}\Delta\epsilon_1)}$$

or with sufficient accuracy

$$\Lambda = \frac{k\pi^2}{4ah^2}(1+\epsilon_0), \text{ which gives } k = \frac{4ah^2}{\pi^2(1+\epsilon_0)}\Lambda \tag{11}$$

where h is the thickness of the compressed gel plate in centimeters; ε_0, the voids ratio corresponding to the thickness h; Λ, the empirical constant in formula (5), and a, the change in the voids ratio caused by a change in pressure of 1 gram per cm.^{2} The value of a can be calculated by formula (10) from Δc, which is the change in concentration due to a pressure change of 1 gram per cm.^{2} at the concentration c.

Swelling of Three-Phase Systems.

In drying out a two-phase system, a fairly well defined point is reached at which air penetrates into the system, and a further contraction of the system almost ceases, although the water content continues to decrease. Beyond this point, the color of the material may grow pale, and air enters the system as a third phase. While the surface tension of water can only exert an influence on the exterior surface of a two-phase system, it now becomes a factor in the interior of the system near the points of contact of the colloid particles. But since one may consider a two-phase system to be a three-phase system with a very large surface area, the preceding comments apply also to the three-phase system.

Summary.

The energy of a two-phase system of given concentration is composed of two parts, mechanical energy and physico-chemical energy. The former represents the equivalent of previous mechanical compression of the solid phase and can be compared with the energy stored in a compressed spiral spring. The latter is the energy equivalent of the physico-chemical interaction of the solid and the liquid phase. The heat of swelling is due to changes in both forms of energy, and can be calculated from the change in the relative vapor pressure, according to the experiments of Katz and others. The change of the relative vapor pressure must, therefore, indicate the change of both forms of energy.

Katz has developed the following conception: *the difference in swelling pressure,* as calculated from the change in relative vapor pressure, is identical with the *difference between the initial and the final swelling pressures measured by mechanical means.* It should, therefore, be possible to transform the entire heat of swelling into mechanical work by means of suitable apparatus.

Against these views the following arguments were presented:

(a) The experimental proof that of two identical clays at the same concentration, one can exert a large swelling pressure and the other no pressure at all (Fig. 10). Since the clays differed only in the amount of inherent mechanical energy, the physico-chemical energy of the two systems could not have had any influence on the swelling pressure in this case.

(b) The experimental proof that the relation between concentration and swelling pressure of fine disperse systems, is governed by the same laws as the relation between concentration and pressure for coarse disperse systems, whose physico-chemical energy is small in comparison to the mechanical energy.
(c) Experimental data that the swelling pressure of a gelatin sample calculated from the relative vapor pressure, is considerably greater at higher concentrations than the directly measured swelling pressure.
(d) The experimental proof, that the time rate of swelling of gelatin follows almost exactly the laws which hold for coarse disperse two-phase systems (Fig. 15).

Since these arguments cast serious doubts on the existing theories of the swelling process, it is recommended that further experiments should be made along that line.

The swelling capacity and the elastic properties of elastic gels (gelatin, rubber, etc.) and of inelastic gels (most clays, silica gel, etc.) differ only in the relative amount of irreversible concentration changes. The author, therefore, proposes that the nomenclature be changed from inelastic and elastic to perfectly and imperfectly elastic gels. It was pointed out that gels consisting of discrete particles must be classified as imperfectly elastic for mechanical reasons. Therefore it may be concluded that perfectly elastic gels contain colloidal particles in a skeleton-like structure.

Besides being perfectly elastic, gelatin possesses two other properties which lead to an assumption of a sponge-like structure: (1) The type of relation which exists between permeability and concentration; and (2) the results of the calculations of the average width of the water channels.

A method has been described for calculating the coefficient of permeability of a gel from the time-rate of swelling.

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On the Rubber-like and Liquid-crystalline States of Matter, in Connection with the Classification of Crystals and Molecules According to Their Vectorial Fields *

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Rubber is highly valued in industry, and not only would it be very important to obtain other substances in a rubber-like state, but in my opinion suggestions as to possible methods of doing so would be welcome. This paper deals with a description of such possibilities.

I have succeeded in obtaining, in an *unstable* rubber-like state, the element—sulfur, and also a compound, silk-fibroin; experiments on prolonging the stability of the rubber-like state, are in progress.

The first part of this paper treats of the classification of crystals and molecules according to the shapes of their vectorial fields. The second part deals with the rubber-like state of matter. Substances of great importance for applied colloid chemistry, such as rubber, natural silk, resins, lacs, lubricating oils, etc., belong to the two classes of this classification.

These substances, very valuable technically,† may also possess the so-called liquid-crystalline state.‡ In view of the importance for applied colloid chemistry, of the knowledge of this state, it is essential to dwell briefly in the first part of this paper on the nature of the liquid-crystalline state of matter.

I. Classification of Crystals and Molecules

The Three Classes

As far back as 1906,§ I arrived at the conclusion that the disperse phases in colloidal solutions of *solid* substances in liquids, consist of ultramicrocrystals and their aggregates. This conclusion was based on the experimental study of precipitation processes of numerous solid substances, and on the establishment of the fact that, by means of a *colloidal* "nucleus," supersaturation in the solutions may be eliminated.

Many logical consequences resulted from this conclusion, of which one is of interest for the present paper, viz. that which is concerned with the structures of the aggregates of ultramicrocrystals. These structures can be easily deduced from the structures of the aggregates of crystals of coarse dispersity, i.e. from macro- and microcrystals; the latter structure being long well known to the geologists and mineralogists. A brief quotation from Otto Lehmann's book [1] will suffice for the illustration of this fact.

* Translated from Russian by Mrs. P. P. von Weimarn.

† D. Vorländer has recently established the possession by certain resins and lacs of the liquid-crystalline state. *Z. angew. Chemie*, 43, 13 (1930).

‡ Compare G. Friedel's paper, "The Mesomorphic States of Matter," in Vol. I of this series.

§ See my paper in Vol. I of the present series.

"Manche Gesteine (z.B.Gneis) zeigen eine eigentümliche *Schieferstruktur,* welche dadurch zustande kam, dass feine kristalline Blättchen (Glimmerblättchen) bei Deformation der Masse im weichen Zustande aus einfachen mechanischen Gründen sich parallel richteten. Jedem Petrographen ist ferner die sog. *Fluidalstruktur* mancher Gesteine bekannt, welche durch Parallelrichtung mikroskopisch kleiner nadelförmiger Kriställchen beim Fliessen der noch weichen Gesteinsmasse bedingt wurde. Würde man einen Haufen langer Drahtstifte zwischen zwei Brettern, von welchen das eine in derselben Richtung hin- und hergeschoben wird, hin und herwälzen, so würden die Stifte bald alle parallele Stellung annehmen."(P. 21.)*

As far back as 1835, long before O. Lehmann, M. L. Frankenheim [2] classified crystal-aggregates into those composed of *grains,* of *lamellae* and of *fibers.*

Assuming the crystallographic designations,† of crystals strongly drawn out in one direction, as *negative* crystals, and of those strongly flattened, as *positive* crystals, I proposed [3] to call those structures which are formed by the negative crystals, *negative fluidal structures,* and those formed by the positive crystals, *positive fluidal structures.*

Thus crystals may be arranged in three classes: To the first, belong those crystals in which not one of the three dimensions shows any great development in comparison with the other two. I called them *neutral* crystals. The second class comprises crystals with one dimension less developed than the two others. As extreme representatives of this class may serve the *finest lamellae.* By the third class are embraced crystals with one dimension highly developed at the expense of the other two. Extreme representatives of this class are crystals *drawn out into finest fibers* or fibrils.

When we pass from macrocrystals to microcrystals which are in suspension in solutions, it becomes impossible to consider them separately or independently from the envelope of the solution adherent to their surfaces, or better, from the "atmosphere" of the solution.

M. L. Frankenheim [4] had already pointed out that suspended crystals, on precipitation, form aggregates in which the individual crystals sometimes are distributed parallel to each other. In my work upon the ultramicroscopy of crystallization phenomena, carried out as far back as 1911-1912,[5] I have explained that Frankenheim's observations were based upon the presence around each crystal, of "vectorial fields" or vectorial atmospheres of the solution, which act when the crystals approach sufficiently close to each other, and effect their parallel orientation. A single quotation from my earlier paper suffices to show my conception of a "vectorial field."

"A crystal, floating in its dispersion medium, is surrounded by a film of this dispersion medium. The thickness of the film, as well as the degree of its saturation with the substance of the crystal, are different on every face, and in general, they are dependent upon the direction of the faces in space.

"Owing to differences in concentration, it is evident that in the film of the solution which is surrounding the crystal floating in its saturated solution, diffusion currents will arise, which are also vectorial.

"Thus owing to the action of a 'crystallisation force' upon the nearest parts of the dispersion medium, a 'vectorial field' is created around a crystal, which field is of dimensions lying within the limits of vision of the *most powerful* optical apparatus.

"When several crystals are floating in the dispersion medium, saturated with the sub-

* Many rocks (e.g. gneiss) exhibit a characteristic *shaley* structure, which developed because the tiny crystalline flakes (mica flakes) arranged themselves in parallel layers in pursuance of simple mechanical laws when the soft magma was deformed. Petrographers are also familiar with the so-called fluid-like character of many rocks, consequent upon the parallel arrangement of microscopically small needle-shaped crystals in the still fluid magma. Thus, if a heap of wire rods were moved to and fro between two boards, one of which was shoved to and fro in the same direction, the rods would soon assume a common parallel direction.

† Compare p. 42 of my paper in Vol. I of this series.

stance of these crystals, then prior to becoming grown together in parallel positions, *they will under the influence of their vectorial fields, orientate themselves at a certain distance from each other, in more or less strictly parallel positions.*

"Positions, corresponding to the equilibrium of crystals in an aggregate are not immediately reached by the crystals; and prior to becoming grown together parallelly which involves a squeezing out or breaking off of the films of the dispersion medium surrounding the crystals, *the crystals at some distance are already arranged according to the laws of their symmetry.*" (Reference 5, p. 2144.)

The distribution of forces in the vectorial fields of *neutral* crystals may be compared to an ellipsoid with its axes differing from each other by an insignificant amount. In the *positive* crystals, one axis of the ellipsoid is too small when compared with the two others; whilst in the *negative* crystals one axis is extremely developed in comparison with the other two.

Of course, if macrocrystals of the positive and negative classes form positive and negative structures, microcrystals will do the same. However, these structures are of the most interest when crystals are of *ultramicroscopic size.* When the distance between the surfaces of the ultramicrocrystals in the aggregates is less than half a wave length of light, it is impossible to observe them separately even by means of the most powerful ultramicroscopes, to say nothing of a mere microscopic examination. The vectorial fields around the ultramicrocrystals being in liquid state, the whole aggregate of ultramicrocrystals will be semi-liquid or liquid; and under microscopic observation, the aggregate will *seem* homogeneous.

Neutral ultramicrocrystals form semi-liquid or liquid spherolites, or formations approaching spherolites (*neutral fluidal* structures). *Positive* and *negative* ultramicrocrystals form correspondingly *positive* and *negative liquid* or *semi-liquid* fluidal structures.

All these three categories of semi-liquid or liquid structures represent three classes of the aggregate liquid-crystalline state; the universality of which state I proclaimed as far back as 1908.[6]

The importance of the rôle played by this state in dispersoidology is also evidenced by the fact that it occupies considerable space in the last edition (1927) of Wolfgang Ostwald's admirable book "Die Welt der vernachlässigten Dimensionen."

However, Wo. Ostwald holds (*loc. cit.* p. 160) that this state "can be assumed only by certain substances, and not by any means by all." The view of Wo. Ostwald upon this kind of liquid-crystalline state which is caused by a special structure of the molecules of substances (see below), is quite correct and perfectly coincides with the view expressed by me in 1908.*

On the other hand, with respect to the *other* kind of liquid-crystalline state, which I have called the *aggregate* liquid-crystalline state, the views of Wo. Ostwald are in disagreement with mine. I maintain that this is a ***universally possible*** state.

Of course it is more difficult to obtain negative or positive structures of the aggregate-crystalline state, in substances which are yielded under ordinary conditions in neutral crystals, than in those substances which under ordinary conditions give typical positive or negative crystals. However, under the conditions of very great supersaturation,† the former substances are yielded in the form of ultramicroneedles or ultramicrolamellae, instead of in neutral ultramicrocrystals. They are apt to yield extended or flat crystalline formations, especially from extremely viscous media containing high-molecular

* See Reference 6, II.
† See my paper in Vol. I of this series.

substances in solution. Moreover, in those cases when *neutral* ultramicrocrystals arise, conditions may be also created, under which *neutral* structures of the *aggregate*-crystalline state (liquid and gelatinous spherolites) will form.

Hence as far as universality goes, there exists a similar relation * between the two kinds of the liquid-crystalline state as between the two kinds † of the colloidal state, dispersoidal and solutoidal.

Now one more step is left, *viz.* to pass from ultramicrocrystals to molecules and to arrange them also into three classes, according to the distribution of intensities of forces, in the *vectorial fields* of molecules.

In one of my papers,[7] dealing with the liquid-crystalline state, I wrote that negative and positive fluidal structures are appropriate not only to extended or flat ultramicrocrystals, but also to extended and flat molecules, as was supposed long ago by Otto Lehmann.‡ This classification received further development in one of my papers dealing with rubber.[8]

Let us designate as the "*molecular*" melting temperature of a solid substance, that temperature at which this substance is disintegrated into *detached* molecules or, in extreme cases, into very small associations of molecules. By the "aggregate" melting temperature of a substance, we mean the temperature of fusion or in certain cases only of softening of the substance; at which temperature certain substances are disintegrated into lamellae of monomolecular thickness or into fibrils possessing a cross-section which is equal to that of molecules.

If, for clearness' sake, we imagine the distribution of intensities in the vectorial fields of molecules (of Class I) of a substance with one usual melting point, to be in the form of an ellipsoid not very greatly differing from a sphere, then we shall be able to understand easily that, upon reaching the melting point, a crystal disintegrates into separate molecules.

Now if we imagine the distribution of intensities in the vectorial field of the molecule (molecules of Class II) of a certain special substance as an ellipsoid flattened to the form of a thin plate, then it will be easily understood that at a certain temperature, lower than the usual melting point, there will ensue a disintegration of the crystal of the substance under discussion, into lamellae, i.e. this substance will possess one more special temperature, which may be called "the temperature of the dispergation of substance into bidimensional *vectorially* constructed aggregates of molecules.

Finally, if molecules (of Class III) of a certain other special substance possess vectorial fields, the distribution of the intensities of which may be represented in the form of a thin ellipsoid drawn out like a needle with ellipsoidal ends, then before reaching the usual melting temperature, the crystals of the substance under discussion will disintegrate into fibrils; this temperature may be called "the temperature of the dispergation of a substance into monodimensional *vectorially* constructed aggregates of molecules."

The temperatures of *bidimensional* or *monodimensional* dispergation of substances, are their "aggregate" temperatures of fusion. Naturally these liquids are different in their properties (viscosity, etc.) from ordinary liquids, with molecules of the first class. Besides, their optical properties evidently require that they be considered as belonging to the positive and negative classes of the liquid-crystalline state.

By no means all substances having extended or flat molecules can be brought into the liquid-crystalline state by mere heating, because some of them

* See Reference 6, II.
† Compare P. P. von Weimarn, *Rév. gén. des Colloïdes*, 7, 153, 1929.
‡ Otto Lehmann, l. c. "Flüssige Kristalle," p. 21.

undergo chemical decomposition before they reach their "aggregate" temperature of fusion. However, by means of liquids or solutions of other substances, these substances can be dispergated into the bidimensional and monodimensional aggregates of molecules.

It should be noted that in recent times, Ernst Alexander and Karl Herrmann [9] have developed a theory of the liquid-crystalline state, the basic principles of which theory almost coincide with the above views advanced by me. These investigators have, in addition, given a detailed classification of these monodimensional and bidimensional formations.

Substances which, according to the form of their crystals or to their molecular fields of forces, may be classified with Classes II or III, are exceedingly important for industry. Substances of Class II possess valuable lubricating properties, and their crystals display high *lamellar* cleavage; as for instance, graphite, lubricating oils, etc. Rubber belongs to Class III as do also such technically important substances as silk, cellulose, etc. Crystals of this class possess high *fibril* cleavage.

The Tendency of Crystals and Molecules, Belonging to Class III, to Form Jellies and Spiral Structures. Fibril Cleavage of Rubber; the Molecules of Rubber Are Spirals

Under suitable conditions of crystallization from solution, substances of *all* three classes may effect the gelatination of the whole solution.[10]

However, whilst a substance belonging to the third class establishes gelatination, substances of the first and second classes, under the same conditions, are precipitated from the solution to the bottom of the container in precipitation forms other than jellies. For instance, in the precipitation from aqueous reacting solutions, of the needle-shaped crystals $CaSO_4.2H_2O$ and $SrSO_4.2H_2O$, there are formed microscopic jellies, whilst under the same conditions, from $BaSO_4$ no jellies are obtained, etc.[11] But the $CaSO_4.2H_2O$ and $SrSO_4.2H_2O$ needle-shaped crystals are far from being extreme cases of negative crystals. And it may be assumed that under conditions equal for the substances of all three classes, the more pronounced the negativity of the crystals, the more easily gelatinization will occur upon crystallization of the substance.

Extremely negative crystals of the shape of hairs or threads, have a distinct tendency to become curled; i.e. within the solution they cannot keep their straight extended shape. One of the main reasons for this lies in the tendency of the layer of the liquid solution adherent to the surface of such a thread, to reduce its surface tension to a minimum. Therefore, these extremely thin crystalline hairs and threads become curled into different spiral shapes, regular as well as irregular.

The fibril cleavage of rubber may be demonstrated without any difficulty, by the examination under the ultramicroscope of Hevea-latex and Hevea-vultex [12] coagula,* suitably prepared and stretched out more or less strongly. The photo-ultramicrographs (magnification 1,140, ultra-condensor Leitz) in Figure 1 (latex) and Figure 2 (vultex) clearly demonstrate the existence of fibril cleavage in the rubber coagula.

In the direction perpendicular to the direction of stretching, the rubber coagula become divided relatively easily into detached threads. By study of the stretching phenomena of rubber coagula under the ultramicroscope, it

* On the preparation of these coagula, see my papers indicated in the references under No. 2.

was learned that *extremely* fine threads obtained from these coagula possess high elasticity.

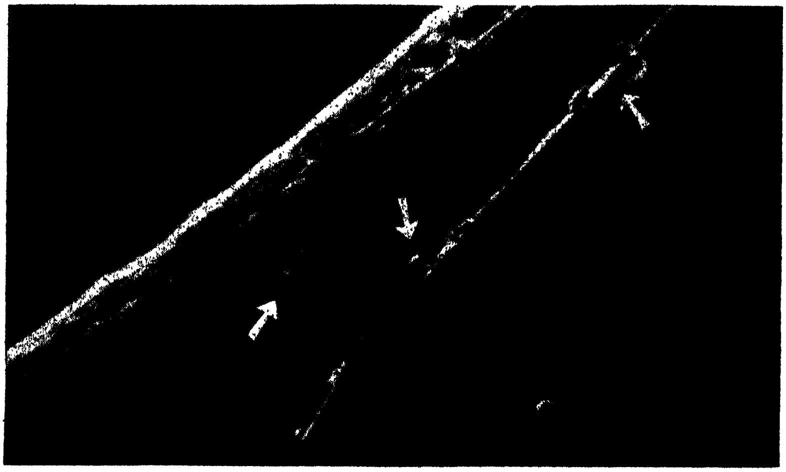

FIG. 1. × 1,140.

And when we see that rubber may be drawn out into threads of such an extreme fineness that even under the most *contrasted* ultramicroscopic illumination of the preparation (see Figure 3 and Figure 4, following the indica-

FIG. 2. × 1,140.

tion of the white arrow) and with the *highest aperture possible* of the objective, these threads are only just visible, or their middle (the finest) parts are ***even absolutely invisible,***† then we must conclude that ***the rubber molecules themselves have a spiral structure.***

† After the lapse of some time, if the stretching be continued further, the thread breaks up at this middle part; the broken ends become somewhat thicker and curled spirally into a small lump (Fig. 3).

FIG. 3. × 2,375.

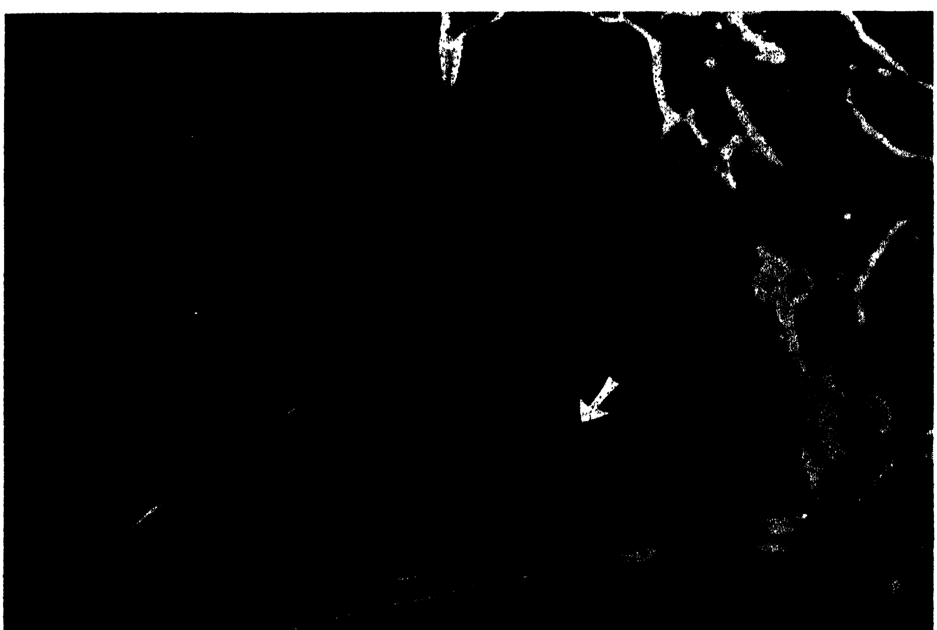

FIG. 4. × 2,375.

It is only natural that very long molecules, if in a free state (for example in a solution), must become curled in one way or the other.

It is of interest to note that almost immediately after the publication of the above conclusion of mine, on the necessity of assuming a spiral structure for a rubber (not stretched) molecule, K. H. Meyer and H. Mark [13] arrived at an analogous conclusion by quite different procedure, *viz.* on the ground of the structure-chemical analysis of an X-ray diagram of rubber.

K. H. Meyer [14] stated his opinion thus: "Die gespannte Kautschukkette hat die Tendenz sich einzurollen, und dass die aneinander haftenden Ketten und Micelle beim Kontrahieren die makroskopische Kontraktion des Kautschukfadens bewirken." *

Thus by two quite different methods the conclusion has been reached that the structure of a rubber molecule is spiral.

II. The Chief Reasons for the Rubber-like State of Matter

A system possessing the high elasticity of rubber must have the following structure: (1) The *primary* structure elements of such a system must possess the form of spirally curled fibrils; (2) the interfibril dispersion medium must be extremely viscous (plastic) and permit the fibrils, after the stretching out of the system, to become curled when the system has been released from tension.

The primary structure elements may of course give rise to secondary, tertiary, etc., structures; but all these structures must possess the possibility, found in their *primary* structure elements, of becoming spirally curled after the system has been released from tension, because, as I am convinced, only through the straightening and curling of the spiral structure, are those great extensions and contractions achieved which are found in rubber.

The interfibrillar viscous dispersion medium may have the consistency of plastic oil, or that of a weak jelly, but in the case of its being a jelly, it must, during the stretching out of the system, be able to dispergate into a plastic condition.

In the case of rubber, we have also spiral fibrils of a solid polymeride and an extremely viscous liquid (consisting of vectorial particles of high dispersity extended in one direction) of a "liquid modification" of rubber (which modification is more fusible, and more soluble). Only an extremely protracted transformation of this "liquid modification" into a solid one, produces for a sufficient length of time in the rubber that elastic state which is so important for practical purposes.

The question now rises concerning the essence of the "liquid modification" of rubber. In accordance with the old views, it is now assumed (Wo. Ostwald, J. Duclaux, E. Hauser, etc.) that the difference between the solid and liquid modifications of rubber, lies in the different degrees of polymerization of the C_5H_8 molecule; the solid modification has a considerably greater polymerization degree than the liquid one.[15] The relation between the two modifications has been expressed by Paul Bary as follows:

$$(C_5H_8)^{\alpha} \rightleftarrows \frac{\alpha}{\beta}\,(C_5H_8)^{\beta}$$

where $\alpha < \beta$.

* "The tendency is for stretched rubber-chains to curl up, and the contraction of mutually adhering chains and micells determines the macroscopic contraction of rubber."

Of course, as with sulfur, for instance, no doubts can be entertained as to the existence of different modifications of rubber, with differing melting points. But it should be also taken into consideration that the formation of a viscous-liquid part in rubber, may be accounted for also by the fact that rubber is a substance the molecules of which belong to Class III of my above-described classification. And considered in the light of this classification, the viscous-liquid part may consist also of short fragmentary pieces of fibrils of molecular thickness, which are distributed in relative disorder with regard to each other. As stated above, substances possessing molecules of Class III have a temperature of monodimensional dispergation or an "aggregate" temperature of fusion or of softening.

This temperature, lying for rubber probably somewhere near 0° C., will be its *"aggregate"* temperature of fusion (or solidification), whereas its *molecular* melting temperature (*i.e.* the temperature of the disintegration of the fibrils into molecules) will be approximately 200° C.*

It is clear that a substance composed of molecules possessing the distribution of intensities in its vectorial fields described above, will easily change its consistency under the influence of mechanical "work"; because the breaking of fibrils into smaller ones is tantamount to approaching the liquid state. On the contrary, every movement, *e.g.* by means of stretching the substance, of short fibrils in a direction parallel to each other, gives them more chance to unite into longer fibrils by way of a mutual union of the molecules at the regions of the vectorial fields with highest intensities.

Rubber is usually applied and treated at temperatures lying below those corresponding to the destruction of the connection at the regions of high intensities of the vectorial fields of its molecules (it is the melting temperature for these regions), and above the temperature of the disturbance of the connection for other regions of the same vectorial fields (*i.e.* the melting temperature for these regions).

"Heat inhomogeneity" (in the sense of J. Clerk Maxwell) for substances possessing such extremely unequal distribution of intensities in their vectorial molecular fields, plays a special rôle in the sense of influencing the general consistency of the system. The molecules which are hotter (the temperature measured by the thermometer is constant) give the liquid part, the cooler ones work as factors for the union of the fibrils of monomolecular thickness into thicker fibers.

Systems, possessing molecules of the character discussed above, remain with ease (completely or only in certain places of the system) in overcooled conditions, and these conditions may be changed by mechanical influences of different character.

With this view, it is not difficult to understand that rubber can be considered also as a substance, which under temperatures lower than the molecular temperature of fusion, is in an aggregate fluid-crystalline state.

The reverse conclusion, *i.e.* that every substance, which is in the aggregate liquid-crystalline state, should possess the elasticity of rubber, would be quite erroneous.

III. Instances of the Rubber-like State

A. Elementary Body: Sulfur

As far back as twenty years ago,[16] I obtained sulfur in an unstable rubber-like state. By pouring in a thin stream, liquid sulfur heated above 400° C.

* *"Aggregate"* as well as *"molecular"* temperatures of fusion, differ of course for every sort of rubber, and vary under the influence of admixtures.

into liquid air, the sulfur is obtained in the form of threads of 0.5 to 1 mm. in diameter. The threads, when taken out of the liquid air, are perfectly solid and brittle. With the rise of temperature * to a certain degree, the threads acquire extremely high elasticity similar to that of rubber. The surface of the threads looks as if polished, and the light is perfectly reflected. In transmitted light the threads are light yellow; in reflected light they appear light gray. They are perfectly transparent and have no traces of opalescence. The results of my experiments, showing the degree of elasticity of these threads, are summed up in the following table.

Initial Length of Threads	Diameter of Threads	Maximum Stretching	Relation of the Stretched Length to the Initial Length of the Thread
8 cm.	About 1 mm.	62 cm.	7.7
8	" 1	45	5.6
3	" 1	10	3.3
4	" 1	26	6.5

Hence the mean relation of the length of the stretched thread to the initial length is equal to 5.5. The thread almost completely contracts to its initial length when the stretching exercised is somewhat less than that required for the maximum stretching. This elasticity however lasts only for a short time, not more than half an hour, after the thread has left the liquid air. The threads then become dim, though they remain translucent; and they assume the state known as the plastic or viscous state of sulfur. After the lapse of 24 hours, the threads lose their plasticity and become quite opaque. They also become brittle, and the color of their breaking surfaces is a light yellow.

Undoubtedly no substances exist in nature whose molecules have vectorial fields of forces comparable mathematically to spheres, *i.e.* it is impossible to have an absolute equality of intensities of forces at any point of the vectorial field of molecule.

Naturally the fields of forces in sulfur molecules are far from spherical. It is known that sulfur atoms readily form stable molecules with different numbers of atoms. And this is a direct indication of the unequal distribution of forces in the atoms of sulfur, as well as in its molecules.

Under a rapid cooling of a thin stream of liquid sulfur from +400° C. to —200° C., some of the molecules fasten to each other at the points in which the intensities of their vectorial fields of forces are a maximum; at these points the molecules unite and the thinnest possible threads are formed (of a molecular thickness or a little above it). Another portion of the molecules give, at a low temperature, highly disperse glass.

As the temperature rises, this glass melts into a viscous liquid or plastic gelatinous mass. Owing to the presence between the spiral fibrils of sulfur, of a mass possessing such a consistency, a system arises which for a time is endowed with the high elastic properties of rubber.

But the transition of this disperse system, representing very unstable states of sulfur, into a system of a coarser dispersity, proceeds very rapidly, with the loss of the rubber-like state which lasts only for half an hour.

* In this case also there exists a special temperature, the "elasticity temperature" as designated by G. S. Whitby. Above or below this temperature, the elastic properties decrease rapidly. See the interesting work of G. S. Whitby and his pupils, in "Studies of Organophilic Colloids," "Colloid Symposium Monographs," New York, Chemical Catalog Co., Inc.

B. COMPOUND: FIBROIN

Through the photo-ultramicrographs in Figures 5 and 6[17] (cellulose) and Figure 7[18] (natural silk) it is convincingly demonstrated that cellulose and silk fibers, swollen up in concentrated aqueous solutions of salts, represent a collection of the finest fibrils curled into spirals. Between these fibrils is enclosed a more or less viscous salt solution, containing cellulose or silk in a colloidally dissolved state.

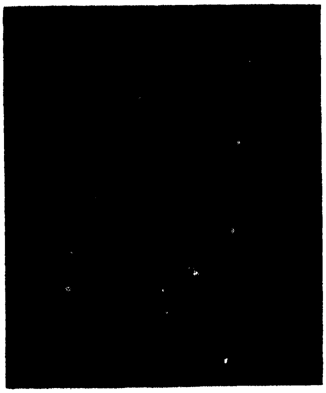

FIG. 5. × 200.

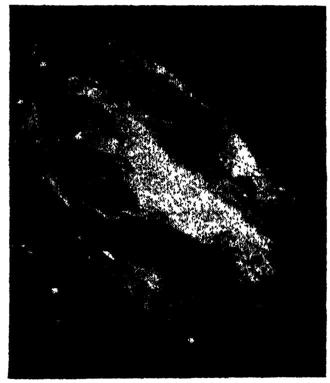

FIG. 6. × 200.

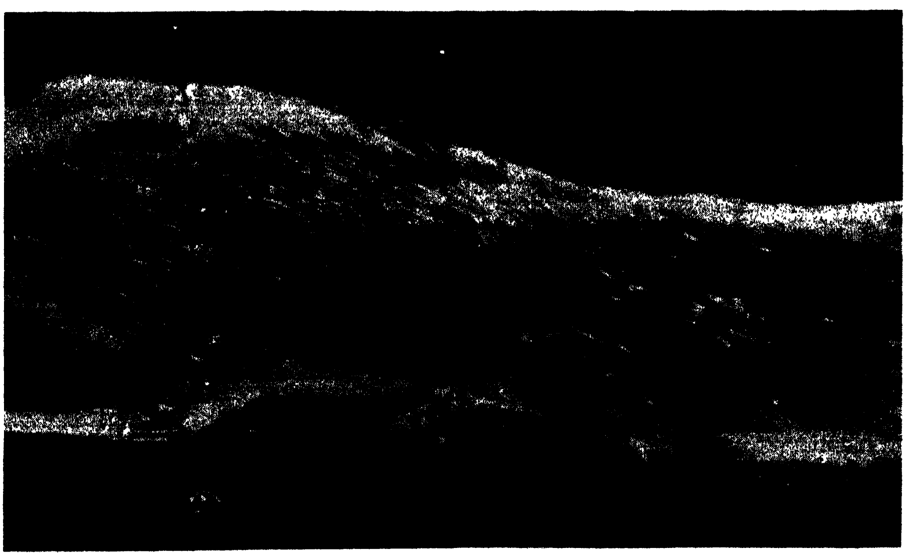

FIG. 7. × 1,200.

Experiments on stretching the cellulose fibers gave no successful results, because the fibers could not stand stretching without being torn or broken. But it is certain that the elasticity of swollen cellulose fibers is greater than that of unswollen fibers, *provided the spiral fibrils are preserved intact.*

Five years ago I obtained for the first time natural silk in a rubber-like

state, which however was not stable. The experiments were performed in two ways: either by the swelling up to a suitable extent of silk threads in concentrated aqueous solutions of neutral salts, or by obtaining, by various methods,* from silk solutions, ropy-plastic coagula-doughs of silk. On ageing, these coagula pass through the rubber-like state.

As the highly elastic state of silk is not a lasting one, it persists sometimes only for several minutes, sometimes for several hours; seldom does it last for several days, and rarely in the extreme for about a week.† Thus threads can be obtained from the silk coagula which possess temporarily a high-elastic rubber-like state.

For instance, a thread may be drawn out to two and sometimes to four times its former length, and after being left quiet, it will contract and resume its original length. When such a thread becomes with time more solid and less elastic, then, by subjecting the thread to "mastication," the former elasticity will be recovered by the thread; if the mastication is carried out too strongly, the coagulum may gain in plasticity but lose in elasticity.

Here we have a perfect analogy with the mastication of rubber. However, the rubber-like state of silk coagula happens to be only a transitory state. The elasticity of the coagulum decreases, and when drawn out into a fine thread, the thread becomes solidified, assuming the consistency of threads of natural silk and losing its rubber-like elasticity.

Though it has still been impossible to preserve silk coagula for a long time in the rubber-like state, the study in natural and polarized light of the micro- and ultramicrostructures of silk coagula permits us to draw certain definite conclusions as to the causes effecting the rubber-like state of matter in general.

Threads of silk develop a rubber-like state when, in the process of swelling, a certain part of the silk substance has already passed into an extremely viscous liquid, with fibrils in the form of spirals embodied in this viscous liquid. The thread will begin to display the elastic properties characteristic of the rubber-like state only when the quantity of the spiral fibrils is sufficiently great and when the viscous liquid plays only the rôle of lubricating oil.

When by means of strong mastication, or by further swelling, the quantity of destroyed fibrils increases, a transition from the rubber-like to the plastic state takes place; and when the thread is subjected to stronger stretching (coagulation by stretching) or when it undergoes syneresis, there will ensue a transition to the consistency of ordinary silk thread, with an almost parallel arrangement of stretched fibrils, or a transition to an almost perfectly solid consistency.

A silk coagulum in the relaxed rubber-like state, acts relatively very weakly upon polarized light, and the determination of its ultramicrostructure is very difficult; nevertheless, in spite of these difficulties, its ultramicrostructure is established with certainty as consisting of spirally curled fibrils (Figure 7).

During the stretching out of the silk thread in its rubber-like state, the spiral fibrils become lengthened by stretching, they are brought close to each other, and in some places, where the liquid is squeezed out, they develop vectorial cohesion, which is accompanied by a release of heat; during this process of stretching, the micro- and ultramicro-drops of the viscous liquid

* See my paper on dispergation and aggregation of silk, in the present volume.

† Of all silk coagula, the coagulum "silk + tannin," when kept moist, preserved for the longest time its elastic properties; even after several months this coagulum possessed rubber-like properties to a certain degree; but it is different from the rubber-like state of silk coagulum obtained by means of alcohol and salts-aggregators, inasmuch as the coagulum "silk + tannin" possesses a considerably softer, doughy consistency.

which is between the fibrils, assume the shape of streamlets strongly extended and arranged parallel to each other; i.e. they assume a structure, which is extremely unstable for the liquid state.

As soon as the stretching has ceased, the streamlets of the viscous liquid under the influence of surface energy, tend to assume volumes with the smallest possible surfaces under the given conditions. The stretched-out fibrils become again curled into spirals, breaking up their vectorial cohesion with the adjacent fibrils (as yet not at full strength), i.e. the system practically returns to its initial state, and to its former length.

In the case of silk coagula, the viscous liquid is an extremely viscous colloidal solution of fibroin, which is in the form of high-disperse vectorial elements drawn out in one direction. This colloidal solution either coagulates * into fibrils, or dispergates the remaining fibrils; this depends upon whether the system under discussion tends to aggregation or to dispergation. The rubber-like state of the silk coagulum vanishes in both cases.

Of course not the slightest theoretical doubt can arise as to the existence of factors in a silk coagulum which by delaying the coagulation of the inter-fibril liquid, can prolong the duration of the rubber-like state of silk. The discovery of such factors is a subject for future researches.

On the ground of the study of the ultramicro-structure of silk in an unstable rubber-like state, and of the structures of the *aggregate* liquid-crystalline state of silk,[19] I conclude that the rubber-like state of substances is dependent upon whether the molecules of this substance belong to Class III of the above classification.

However, the existence only of an unequal distribution of intensities of forces in the vectorial fields of forces of molecules, is not a sufficient condition for obtaining *stable* spiral fibrils. For this purpose, it is necessary that the greatest intensity in the field of forces of a molecule is not only relatively (in relation to the other points of this field) but also *absolutely* great. Otherwise the spiral fibrils will possess not sufficient tensile strength, and may even be broken up with comparative ease on stretching.

The greatest intensities of the field of forces in rubber molecules are also absolutely very great; and this accounts for the high tensile strength of rubber. Neither rubber-like sulfur nor rubber-like silk possesses such great tensile strength.

Thus in my opinion, the problem of obtaining substances in a *stable* rubber-like state may find its solution, when from a rich stock of organic substances, those will be tried which possess molecules of Class III, the greatest intensity of the strongly extended vectorial fields of forces of these molecules being in addition *absolutely* great.

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Editor's Note.

The spiral arrangement of molecules here pointed out has an important cytological and genetic interest; for during mitosis the gene-string apparently coils up when the "loose skein" passes over into the "tight skein" within the chromosomes (*see* paper by Alexander and Bridges in Vol. II of this series).

When crystals reach a certain size, their decrease in kinetic activity permits surface tension forces to gather them into aggregates. In the presence of viscous or protective substances, these aggregates may persist (*see* paper by Endres in Vol. I of this series; *also* J. Alexander, First Colloid Symposium Monograph, 1923).

Surface and Catalysis *

By Edward Frankland Armstrong, Ph.D., D.Sc., LL.D., F.R.S., London.

The object of this brief article is to indicate in simple language free from obscure technical verbiage, some of the proven facts of the behavior of catalysts in promoting chemical actions. Catalysts are to-day of immense importance in industry; already a considerable number of substances are being manufactured on a large scale with their aid and it is certain that we are only on the fringe of the great possibilities which their application will make feasible.

Substances which are catalysts act in virtue of their surface. A more active catalyst is so in consequence of increasing surface. The preparation, use and behavior of catalysts is entirely a question of surface. The interaction between the substances, whether gases or liquids, which are about to be changed, takes place at the surface, in virtue of it and because of its specificity. Catalysis is thus intimately connected with the colloid state.

In industry a close study of the means of increasing and maintaining the surface of each individual catalyst is requisite—there is no mystery attached to the problem until the question is asked: "Why does the reaction go in a particular manner?" An illustration of the complexity of this interrogation is afforded by the multiplicity of substances to which ethyl alcohol can give rise in presence of different catalysts within the same range of temperature and general conditions. It is the specific nature of the catalyst which determine what the chemical change shall be.

More closely studied from this point of view has been the reaction of carbon monoxide with one, two or three molecules of hydrogen, producing formaldehyde, methyl alcohol or methane respectively. Any desired one of these three products can be made, with the practical exclusion of the others, provided that a suitable catalyst and temperature is selected. A copper catalyst at 300° to 400° C. favors the formation of formaldehyde; to produce methyl alcohol a reduced basic zinc chromate is necessary at 300° to 350° C., whilst for methane the best catalyst is nickel at 150° to 200° C. The reactions are carried out at fairly high pressures.

The most efficient catalysts are those having a capillary structure, thus exposing the maximum surface per unit of mass.

There is no doubt that a colloid sol should represent initially the most active type of catalyst, the surface available being at a maximum and, in a sense, present at each point throughout the volume of the solution. Such systems are, however, so extraordinarily sensitive to slight changes of condition, such as alteration in the acidity or alkalinity of the medium, development of local heat, of chemical action, etc., that the result is partial or complete coagulation with an extreme curtailment of the effective surface.

A finely divided metal held at the surface of a suitable rigid support, although probably possessing only a fraction of the initial transitory activity

* Some aspects of catalysts and surface specificity are considered in Vol. II of this series, especially in Chapter I. J. A.

of the same metal in colloid sol form, preserves its activity at a much more nearly constant level. Such a catalyst may indeed become coated with an impermeable film of deposited coagulated colloidal impurity (a "catalyst poison") but its surface cannot be altered by its own shrinkage unless in a relatively very small degree. In industrial practice the most active catalysts are obtained by depositing a thin film of the metal on a catalyst support of a permanently porous or spongy structure.

It is desirable to deal in some detail with the considerations affecting the preparation of the active surface. A lump of nickel is inactive; nickel acquires activity to some extent when finely divided by mechanical means and to a greater extent when the division is effected chemically, i.e. by the reduction of a finely divided precipitate of a nickel salt, e.g. of its oxide, or by the alternate electrolytic oxidation and reduction of nickel turnings thereby producing a film of finely divided metal on an inactive nickel support. To effect reduction an elevated temperature is required and this is sufficient to cause sintering, or in other words a partial coalescence of the nickel particles, which has the effect of destroying their primary structure. This evil is largely overcome in practice by precipitating the nickel on a porous support when it becomes much more resistant both to temperature and to many catalyst poisons.

The study of the effect of the co-precipitation of small amounts of other oxides—aluminum, ferric, magnesium—with nickel oxide shows that this has beneficial results on the catalytic activity of the reduced nickel, but larger amounts produce catalysts which are less active. The admixed oxide will tend to separate the particles of nickel oxide and preclude them from coalescing during reduction although it is not present in sufficient amount to cover the whole surface of the nickel. This will tend to increase the surface. When a larger proportion of the admixed oxide is present the surface of the nickel oxide is so coated over that reduction to the metallic state is hindered.

Experiments have established a definite relation between the bulk or apparent volume of partially reduced nickel oxide and its resulting catalytic power. Further the activity is dominated by the condition of the surface layer of reduced nickel and it is obviously this part of the mass which is first reduced to the metallic state.

The action of catalyst promoters is not capable of a general explanation and each instance requires investigation *per se*. In general it may be said that the apparent promotion is due either to the elimination of some secondary action which was affecting the catalyst or to the introduction of conditions which favor the development of maximum surface by the catalyst.

Catalyst poisons may act either by covering up the catalytic surface and preventing contact between the metal and the other interactants—this can easily happen in liquid hydrogenation when coagulable colloid impurities are present—or by definitely and chemically changing the catalytic metal (e.g. hydrogen sulfide, carbon monoxide).

Catalyst poisons of the second type may be further subdivided into those which effect a permanent chemical change in the metal and those which produce only a temporary combination. Change of the former kind, e.g. to an oxide or a sulfide, can only be remedied by what is practically a fresh manufacture of the catalyst, culminating in its reduction to the metallic state, whereas the effect of the other class of poisons can often be removed by eliminating the interacting agent. Thus nickel which has been exposed to the action of carbon monoxide below about 200° C. is deprived of its hydrogenating power owing to its affinity for this compound, but when the latter is

removed from the gases entering the system the nickel recuperates fairly rapidly.

When an active catalyst is used and conditions are regulated to exclude the effect of poisons and side reactions, for the greater part of the change equal amounts of the organic compound are changed in successive equal intervals of time. The change is linear and not logarithmic. This fact has been proved beyond question and is fundamental.

It being established that catalytic action is essentially action at a solid surface at which the metal is maintained in the highest state of molecular activity, it is desirable to form a conception of the changes that take place.

The linearity of the time-hydrogen-absorption curve in cases of hydrogenation in liquid media is held to be evidence of interaction of the organic compound rather than the hydrogen with nickel, because the rate of absorption varies abruptly during the course of hydrogenation of many unsaturated substances containing two ethylenic linkages at or near the point at which the material becomes semi-hydrogenated, and chemical analysis has shown in such cases that the reduction has been "selective," that is the two centres of unsaturation are reduced in number to one before any proportion of the singly unsaturated product is completely hydrogenated. Consequently, the slope of the time-absorption line is definitely correlated with the organic compound present. It is desirable to emphasize this most striking feature whilst at the same time bearing in mind that hydrogen undoubtedly also becomes associated with the nickel.

It is considered that a loose temporary complex is formed between the organic compound and the metal, the forces of attraction being chemical and not physical such as is supposed by the alternative theory of adsorption.* Such a complex is equally prone to break down into its components either those from which it was built up or into any other which its structure makes possible. This has been exemplified in the case of oleic acid: here during partial hydrogenation both the *trans* isomeride, elaidic acid and an *iso*-oleic acid are produced. It is obviously impossible to expect to isolate such a complex, as were it stable, reaction would not take place. The complex enters into further combination with hydrogen which is present in sufficient quantity and the change is effected.

The quantity of hydrogen present at the surface depends on the pressure; to increase it hydrogenation must be effected in closed vessels under increased pressure.

We have no clear picture at present as to why catalysts are so specific, but it is possible that there may be some relation between their surface and that of the organic molecules changed. In the realm of enzymes, which are pictured as small active centres in large colloid molecules,† the rest of which are inactive, it is well known there is so close a relation between the molecular architecture of the substrate and the enzyme that the lock and key, or hand and glove analogies have been widely used to express it. It has been suggested indeed that an enzyme which hydrolyzes a glucoside is itself a carbohydrate unit in a very large colloid molecule. No such relation can exist between active copper and alcohol, but it is possible that visualizing the copper surface as akin to a mountainous district viewed from above by airplane, a particular pattern of peaks and valleys may conform to the size and structure

* For a discussion of this question (chemical vs. physical forces) see Vol. I of this series. Since the attraction is ultimately electronic, the scope given the words "chemical" and "physical" is determinative. J. A.

† Or particles. Enzymes are discussed by several papers in Vol. II of this series (R. Willstätter, A. Fodor, R. K. Cannan). J. A.

of the alcoholic molecule. Conditions will then be favorable for distortion and the storing of potential energy, so that a minimum of energy has to be supplied to break the molecule up or cause it to be rearranged. Speculations on these lines are beginning to be made in many quarters and they are bound to be fruitful.*

The use of catalysts in industry has been greatly stimulated by the improvement in the technique of working at high pressures.

First in importance, the ammonia synthesis of Haber, worked out by the Badische Anilin und Soda Fabrik, and now almost universal, produced a vast literature, including many patents, on the subject of suitable catalysts. Next came the synthesis of methanol, again first achieved technically by the Badische Anilin und Soda Fabrik. This was followed by the work of Patart, who indicated the use of chromates, manganates, vanadates, molybdates and tungstates of metals which, after careful reduction, gave active catalysts furnishing very pure methyl alcohol.

Franz Fischer used an alkalized iron catalyst at 150 atmospheres pressure at 400° to 450° C. to hydrogenate carbon monoxide, obtaining a product which contained alcohols, aldehydes, ketones and aliphatic acids with small quantities of hydrocarbons. The product separates into two layers, the oily one being termed "synthol" and suggested as a motor spirit.

Liquid fuels are also obtained by hydrogenation of coal under 200 atmospheres pressure in presence of hydrated ferric oxide by the Bergius process. The product consists of saturated hydrocarbons, largely aromatic and varying amounts of phenolic substances. The process has been extended to tars from low temperature carbonization either of bituminous coal or brown coal, a very large plant existing in Germany for this purpose. In some cases molybdenum compounds are used as catalysts. Even better results economically are expected from the application of the principle to oil residues and an international syndicate exists to develop this field of hydrogenation.

The knowledge of high pressure technique is now so wide that there are several alternative and highly competitive processes of effecting the ammonia synthesis. The same applies to methanol synthesis from water gas; the product is now advocated as a liquid fuel. Hydrogenation of coal and oil is technically possible; the economic potentialities of the process depend on the general oil position. Though this economic position today is adverse to the success of the catalytic processes, what is important is the fact that the means is at hand, by suitable variation of the catalyst, to make, within limits, products of any desired character either from coal, from low or high temperature tars, or from water gas, that is from coke. The problem of a substitute for oil, should the natural supplies be exhausted, has been solved by the chemist. The problem remains of finding out a good deal more about the properties of gases and mixtures of gases at high temperatures and pressures, and the mechanism of the catalysts.

* Views along this line are advanced in a paper by Alexander & Bridges in Vol. II of this series; also by Alexander, *Science* (N. S.), 65, 62 (1927) ("Kinetic Activity, Oriented Adsorption and Molecular Deformation in Catalysis"). J. A.

Contact Catalysis

By Hugh S. Taylor,

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Contact catalysis is the chemistry of reactions occurring at surfaces. It is this localization at the surface which brings the subject within the field of colloid chemistry since the distribution of the reacting materials between the surrounding phase and the surface is determined by the properties of the surface and the reactant concentrations. Since the reactions are localized at the contact surface it is found to be advantageous in many cases to produce the maximum extension of surface per unit of catalyst mass. Hence, the catalyst frequently assumes a form familiar in the discussion of colloid systems; its surface has properties not normal to systems in the massive form but more and more recognizable as normal in systems in a fine state of division.

Faraday was the first to indicate the zone of adsorbed material as the reaction space of a heterogeneous catalytic action. The kinetic investigations of Bodenstein showed that, in this space, the behavior of the gases could be studied and the influence of concentrations of reactants on velocities in this zone could be experimentally established. Haber's researches on ammonia synthesis showed the beneficial effect of high pressures on the yield of products produced at such surfaces in the case of reactions involving a volume diminution and, as is well known, this led to results of enormous technical importance in the case of ammonia, methanol and higher alcohol synthesis and in the hydrogenation of coal and oils under pressure. Langmuir's studies on surface reactions further defined the reaction zone as a region of adsorbed gas, not, in general, greater than unimolecular in thickness with respect to reacting gases and products. This contribution of Langmuir [1] is the *leit-motif* of all recent kinetic studies of surface reactions and it has now been shown in a great many cases that this method of approach to the kinetics of such reactions is most fruitful.

The pioneer investigations of Sabatier [2] were of a quite different nature. He showed that certain types of reaction could be induced by certain types of contact agent. Thus, metals, and, specifically, Pt, Pd, Ni, Co, Cu, Fe, were agents *par excellence* for reactions of hydrogenation and dehydrogenation. His detailed studies of nickel catalysts in this respect had a two-fold result. They opened up new avenues of organic synthesis. They also taught us much concerning the form of the catalyst and its importance in successful catalysis, the effect of poisons, overheating and the like on the efficiencies of contact agents. Technical studies on industrial processes were simultaneously providing additional data of this kind. Sabatier showed also that oxide catalysts promoted two types of reaction, the one hydrogenation-dehydrogenation, the other hydration-dehydration. Some oxides exerted both influences, some the one and some the other practically exclusively. The use of zinc oxide in technical methanol synthesis can be traced back to these fundamental studies of Sabatier. The use of non-metallic elements such as carbon, iodine and sulfur, as well as metal halides in reactions involving halogenations, supple-

ments the list of catalysts and reaction types to which the catalytic chemist may turn for suggestions to solve a particular problem.

Technical development led to a further major improvement in the technique of catalytic processes. The discovery [3] by the Badische Anilin u. Soda Fabrik through the researches of Mittasch and his collaborators of the importance of minute amounts of addition agents on the activity of catalytic masses, revolutionized the technical application of catalysts and propounded a very attractive theoretical problem for the student of catalyst materials. This problem of promoters in catalytic agents can be illustrated by the query as to why the presence of 1.5 per cent of $K_2O.Al_2O_3$ in pure iron so enhances the activity of the iron for ammonia synthesis that, without it, only meager yields of ammonia are possible, with it a highly profitable industry can obtain. Following the discovery of promoter action in ammonia synthesis, similar applications of promoters to all other types of contact agents followed with conspicuous success. The modern development of a catalytic process follows therefore a stereotyped procedure. A survey is made of the possible types of contact agent for the reaction in question; the best individual in the catalyst type having been selected, an attempt is made to increase its activity by incorporation of promoting agents. These normally serve also to increase the toleration of the catalyst material proper for the poisons and inhibitors of reaction usually or accidentally present in the reacting masses. There is in this procedure, still, much more of art than of science. The central problem, theoretically, why specific contact agents produce acceleration of specific reactions is still unsolved. Something has been learned, however, of the factors which lead to high activity of materials when brought into suitable form.

The Concept of Active Centers on Catalysts.—Adsorption precedes catalytic change. Taylor and Burns [4] showed that with metallic hydrogenation catalysts marked adsorption of gases occurred. Pease [5] studied the relation between adsorption and reaction velocity in detail, with hydrogen and ethylene on copper, showing that high adsorptive capacity was paralleled by high catalytic activity. There was, however, no strict proportionality between the two. The action of high temperatures destroyed catalytic activity proportionally more than it reduced adsorptive capacity. Furthermore, small quantities of poisons, for example, carbon monoxide, which were inadequate to saturate the surface of the copper so far as adsorption was concerned, practically suppressed the catalytic activity. This points to a non-uniform surface. Were the surface uniform, a poison should produce an effect on reaction velocity proportionate to the surface its covers. Pease and Stewart [6] have shown that this is not the case.

The extent of the surface which is active varies with the nature of the reaction catalyzed. There is unequivocal evidence that, in certain reactions, every atom in the surface is active. In others, the evidence is equally definite that only a small fraction of the surface is active. In the former case the reaction is relatively insensitive to poisons, in the latter case extremely sensitive. Hence arises the possibility of progressive poisoning in which, on a given catalyst, different reactions are successively stopped by increasing amounts of poison. The study by Vavon and Huson [7] of a colloidal platinum on which the hydrogenation of propyl ketone, piperonal and nitrobenzene were successively suppressed by addition of increasing quantities of sulfide poisons is a good example of such behavior.

The extent of the surface which is active may also vary with the temperature of the reaction. This is established by the proportionally smaller influence of an irreversible poison on the rate of a catalytic reaction the

higher the temperature. The proportionally smaller effect of a destruction of a catalyst by heat the higher the temperature at which the catalytic reaction is measured also demonstrates the same effect. A heat treatment of copper which practically suppressed its activity for the hydrogenation of ethylene at 0° C. has a very much smaller proportionate effect on the rate of reaction at 200° C.

Quantitative measurements of adsorption and catalytic activity on promoted catalysts have also shown that, in certain cases, the promoter action is to be ascribed to an improvement in the quality of the surface rather than to an increase in the amount of surface. Thus, Russell and Taylor showed that, in the hydrogenation of carbon dioxide to yield methane on nickel and nickel-thoria catalysts, a ten-fold increase in reaction velocity due to the thoria was accompanied by only a twenty per cent increase in surface as measured by adsorption of reactants.

These data connecting reaction velocity and adsorption on various types of catalyst all indicate a surface which is not uniform as to catalytic activity. As has also been pointed out elsewhere,[8] the adsorption measurements alone demonstrate this. The varying saturation capacity of a catalyst for different gases, the varying saturation ratio for two gases on different preparations of the same catalyst, or on the same catalyst before and after heat treatment or poisoning, all confirm the idea of a non-uniform catalytic surface.

A theory of the catalytic surface which takes account of the general behavior and varying activity was presented several years ago by the author.[9] In a metal catalyst, "the surface of the granule may be regarded as composed of atoms in varied degrees of saturation by neighboring metal atoms, varying from those one degree less saturated than interior atoms to those which are held to the solid surface by a single constraint." [10] It was shown that such a concept was in accord with the facts of catalytic behavior, the sensitivity to poisons and heat treatment, the facts of adsorption on such catalysts.

There has been a tendency in discussing this theory to center attention entirely on the most loosely held surface atoms and to imply that the theory assumed that only such atoms possessed catalytic activity. This interpretation cannot be maintained by any one who reads with care the original communications on this subject. In them the varying saturation of atoms in the different faces, of the crystal, in the edges, corners and detached atoms of a catalyst granule is considered as producing a progressive change in catalytic activity. Instances are cited [11] in which practically every atom in the catalyst surface is active [12] and it is emphasized that from the quantitative data on poisoning the surest evidence of varied activity will be obtained. Our own experiments [13] on the high catalytic activity at the boundary edges between copper and copper oxide as well as our discussion of such interface phenomena generally [14] shows conclusively that the original theory included all variations of lattice saturation.

Lattice Catalysts.—When we turn from elementary catalysts such as the metals to catalysts composed of compound materials with ionic lattices such as oxides, halides, sulfates, etc., the surfaces in question contain an additional factor of variability. Such ionic lattices may be regarded as dual catalysts, the surface being composed of metal ion and negative ion. To each type of ion may be ascribed a definite and specific catalytic activity. Examination of the catalytic behavior of the oxides suggests that, on the metal ion, processes of hydrogenation and dehydrogenation occur, whereas, on the oxide ion, the processes are essentially hydration and dehydration. With a given process, the extent of the two alternative changes will be determined by the relative

extent of adsorption of reactant on the two ions, on the relative frequency of the two ions in the surface and on their specific individual catalytic activities. These several factors (extent of adsorption, frequency of ions in the surface and catalytic activity) will be determined by the degree of saturation of the lattice ions, and by the extent to which the ions are already covered by poisons (salts, water, ammonia, etc.). With this concept, the variation in dehydration-dehydrogenation ratio of various oxide catalysts in, for example, formic acid decomposition

$$HCOOH = H_2 + CO_2$$
$$HCOOH = H_2O + CO$$

and ethyl alcohol decomposition

$$C_2H_5OH = CH_3CHO + H_2$$
$$C_2H_5OH = C_2H_4 + H_2O,$$

receives a more satisfactory interpretation than has hitherto been suggested for such reactions.

The dual theory of such ionic surfaces also suggests the solution of a difficulty first raised by Hinshelwood.[15] On the surface of glass in the neighborhood of 280° C. the two alternative decompositions of formic acid occur with nearly equal speeds, but the heats of activation differ markedly ($E_{CO} =$ 16,000; $E_{CO_2} = 28{,}000$ cals.). If the numbers of molecules activated for the two reactions are proportional to $e^{-E/RT}$, then carbon monoxide ought to be produced in overwhelming excess. Hinshelwood therefore postulated that decomposition only occurred when the molecules pass through some unstable phase, and that the phase yielding carbon monoxide occurred more rarely than that yielding carbon dioxide. Such a postulate becomes quite unnecessary when the dual nature of the surface is remembered; each ion has its own reaction and its own activation energy.

It is possible that the decomposing molecules are adsorbed on the two ionic types by two different modes of attachment and that it is to this that the different modes of decomposition are due. The experimental evidence is not yet sufficient to decide this question but is now being sought.

The importance of the anion in determining the relative extents of dehydrogenation and dehydration of an alcohol is well illustrated by data accumulated in Princeton on the decomposition of ethyl alcohol on salts of zinc and manganese. The following table shows that, with each metal, with increase in the valency of the anion there is a progressive change from dehydrogenation activity to dehydration activity.

Catalyst	C_2H_4	H_2	Catalyst	C_2H_4	H_2
ZnF_2	12	88	MnO	5	95
ZnO	9	91	$MnSO_4$	5	95
$ZnSO_4$	22	78	$Mn_3(PO_4)_2$	25	75
$Zn_3(PO_4)_2$	43	57	$Mn_2P_2O_7$	88	12
$Zn_2P_2O_7$	99	1			

Heats of Adsorption on Catalysts.—The study of heats of adsorption of reacting gases on catalytic materials has led to results differing fundamentally from those normally cited in textbooks of colloid chemistry. It is frequently stated that heats of adsorption of gases are usually somewhat greater than the heats of liquefaction of the gas in question. How far this is from the truth in respect to adsorptions on catalysts is evident from the following selection of typical data obtained in studies conducted during the preceding years on this subject.

Catalyst	Gas	Integral Heat of Adsorption in Calories	Pressure Range mm.	Observer
Nickel	H_2	14960	0–760	Dew [1]
	NH_3	11240	0–90	Dew [1]
Copper	H_2	9600	0–760	Beebe [2]
	CO	30000	0–1	Beebe [3]
	CO	11700	0–760	Beebe [3]
	NH_3	9200	0–155	Dew [1]
	H_2	11300	0–0.01	Washburn [4]
	C_2H_4	16000	0–0.01	Washburn [4]
	C_2H_6	11000	0–0.01	Washburn [4]
Iron	NH_3	16000	0–10	Dew [1]
Platinum	H_2	32400	0–0.01	Kistiakowsky [5]
	O_2	161000	0–0.01	Kistiakowsky [5]
	CO	34600	0–0.01	Kistiakowsky [5]
	SO_2	35700	0–0.02	Kistiakowsky [5]

[1] Dew and Taylor, *J. Phys. Chem.*, **31**, 277 (1927).
[2] Beebe and Taylor, *J. Am. Chem. Soc.*, **46**, 45 (1924).
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[5] G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 799 (1930).

It is apparent that in each case the values are many times greater than the heat of liquefaction and are comparable with those of a chemical reaction. Any generalization in colloid chemistry as to heats of adsorption which does not include these possibilities must be regarded as a piece of special pleading not consonant with actual experiment in reference to true reversible adsorptions. In certain cases, notably oxygen on platinum, the adsorption is not reversible at practicable evacuation temperatures. But this is self-evident when the magnitude of the heat of adsorption involved is recognized. Similar high heats of adsorption of hydrogen on zinc-chromium oxide catalysts (20,000-30,000 cals.) have been obtained by Flosdorf.[16]

The Energy of Activation of Catalytic Reactions.—In homogeneous reactions it is known that only collisions between molecules having a certain joint energy, known as the activation energy, lead to reaction. It is of interest to know what influence a catalyst exerts on this energy quantity. This may be deduced for reactions the kinetics and apparent activation energy of which are known, provided the heats of adsorption of the reactants and products are known. The true energy of activation, E_t, of a heterogeneous reaction is related to the apparent activation energy, E_a, by an equation

$$E_t = E_a + \lambda - \lambda'$$

where λ is the energy of adsorption of the reactant, λ' that of a retarding agent in the reaction. This equation can be applied to the hydrogenation of ethylene on an active copper catalyst which reaction was shown by Pease to be proportional to the hydrogen pressure and retarded by ethylene. If we use the data of the preceding table obtained by Washburn for such a copper catalyst together with Pease's value of 11,000 calories for the apparent energy of activation of the catalytic reaction, we find that

$$\begin{aligned} E_t &= 11{,}000 + 11{,}300 - 16{,}000 \\ &= 6{,}300 \text{ calories.} \end{aligned}$$

This small activation energy is of the magnitude one might expect for a reaction proceeding rapidly at 0° C. as Pease's experiments showed. It contrasts markedly with the activation energy of the homogeneous gas reaction

which, according to some data of Pease, amounts to some 35,000 calories and occurs only above 300° C.

An important point in regard to the activation energy of surface catalytic reactions may now be considered. Pease showed that if the activity of a copper catalyst were partially destroyed by heat treatment so that the temperature of measurable reaction rate were increased to 200° C., as compared with 0° C. for the more active material, the kinetics changed. The rate became bimolecular, proportional both to the ethylene and hydrogen concentrations. For such a catalyst he found an apparent activation energy of 10,000 calories. In this case it is evident that the true activation energy must be greater than this by the *sum* of the heats of adsorption of both hydrogen and ethylene. That is to say, it is very considerably greater than the activation energy of the very active catalyst but, with probable values for λ_{H_2} (<11) and $\lambda_{C_2H_4}$ (<16), should be less than that of the homogeneous gas reaction. Should further experiment show this to be a general result, we should have the important general conclusion: *Catalysts reduce the activation energy of chemical reactions, the more considerably the more active the catalyst.*

Specificity of Catalysts.—An extension of the type of work here described will also permit a fuller answer to the problem of specificity in catalytic activity. There is some evidence that part of the answer to the problem of specificity is to be found in the magnitude of the heats of adsorption. The data of Dew [17] on the heats of adsorption of ammonia on iron, nickel and copper indicate that the curves for heats of adsorption against amount of gas adsorbed run approximately parallel to one another, the energy of adsorption being 5,000 calories greater on iron than on nickel and 7,000 calories greater than on copper. If we assumed * for simplicity that the decomposition of ammonia on these metals were unimolecular and that the activation energy were the same for all catalysts it can readily be shown that the rates of reaction would be in the ratio $e^{\frac{5,000}{RT}}:1$ for iron and copper and $e^{\frac{7,000}{RT}}:1$ for nickel and copper. At 800° Abs. these ratios would be $e^3:1$ and $e^{4.5}:1$ or 20:1 and 90:1 respectively. The rate on iron would also be greater than the rate on a non-specific adsorbent (on which the heat of adsorption was approximately the heat of liquefaction) to an extent given by the ratio $e^{\frac{16,000-6,000}{RT}}:1$ or, at 800° Abs., $e^{6.25}:1$. These brief examples should serve to show the importance of a high heat of adsorption for catalytic action.

Heats of Adsorption and the Concept of Active Spots.—For one and the same catalyst it is evident that the data obtained in the study of heats of adsorption provide a thermodynamic picture of the concept of active spots developed by studies of kinetics and of poisons. The data of Dew for the heats of adsorption of ammonia on iron are represented by a curve from which the following data are drawn.

Ccs. Adsorbed	2	4	6	8	10	12	14
λ_{NH_3} Kg. Cals.......	18	16	14	12.5	11.3	10.5	9.9

From these data it is evident that if the activation energy is constant and if the reaction velocity on the surface covered by the first two cubic centimeters be taken as unity, the rates on successive areas of the catalyst cited in the above table will be respectively $e^{\frac{-2,000}{RT}}$, $e^{\frac{-4,000}{RT}}$, $e^{\frac{-5,500}{RT}}$, $e^{\frac{-6,700}{RT}}$, etc. For $T =$

* This is only an assumption since it is already known in the case of platinum [Hinshelwood and Burk, *J. Chem. Soc.*, 127, 1105 (1925)] and iron [Kunsman, *J. Am. Chem. Soc.*, 51, 688 (1929)] that the ammonia decomposition is inhibited by hydrogen, thus increasing the temperature coefficient. At sufficiently high temperatures, however, this inhibitory action ceases (*cf.* Kunsman) and an approximation to unimolecular decomposition must hold.

800° Abs. these are respectively 0.2865, 0.08, 0.03, 0.015. It will be seen that, for kinetic purposes, only the areas absorbing the first four cubic centimeters of gas will have any significance so far as velocity of reaction is concerned. They are the active spots. A poison covering the area occupied by the first two cubic centimeters of gas would reduce the velocity to 28 per cent of the normal.

Pease found that 0.2 cc. of carbon monoxide reduced the rate of hydrogenation of ethylene on a sample of copper at 0° C. to 10 per cent of the rate in the absence of poison. On this basis one can calculate that the copper surface covered by the poison had a net heat of adsorption which was $2 \times 2.25 \times 273 = 1{,}230$ calories greater than the areas next in activity.*

If, as seems possible from the data of an earlier section dealing with the true heat of activation, this latter quantity becomes greater the less active the catalyst area, it is obvious that the rates given in the preceding paragraphs will be still further reduced in comparison with the most active area. On this basis, the concept of active spots, of poisons, and of sensitivity to heat treatment become alike thermodynamic necessity.

Poisons.—In contact catalysis the term "poison" is applied to any material which reduces the reaction velocity of the process. Poisons may be "permanent" or "transitory." [18] The permanent poisons require that the contact mass must be renewed before activity is regained. The transitory poisons are those which are only effective so long as they are present in the reacting system. It is now agreed that the action of poisons is to be ascribed always to the diminution of the active catalyst surface by the poison. The reduction may be permanent, either mechanically or where the chemical reaction occurring is irreversible under the experimental conditions. It may be temporary, due to preferential adsorption of the poison on the catalytic surface; if the poison can establish with the surface a reversible chemical reaction, temporary poisoning may also result.

The quantitative study of poisoning has led to a fuller appreciation of the properties of the catalyst surface. It has been known, since the time of Faraday,[19] that minute amounts of poisons had very material influence on reaction velocity; this has been an important factor in many technical developments. Maxted [20] pointed out that the decrease in occlusive power of palladium by poisons was always considerably less than the decrease in catalytic activity. The studies of Pease and his students on the hydrogenation of ethylene on copper in presence of mercury and carbon monoxide as poisons made this observation quantitative. Pease and Stewart [21] showed that the adsorption of 0.01 cc. of carbon monoxide on a copper catalyst reduced the reaction velocity to less than 15 per cent of the normal velocity although the adsorptive capacity of the sample for hydrogen and ethylene was many hundredfold the volume of poison used. It is apparent that the surface covered by the poison must in this case be responsible for the great bulk of the normal reaction rate and that the gas adsorbed on the residual surface must react relatively extremely slowly. It is evident how closely this conclusion agrees with that reached in the preceding section indicating a surface of very varied activity. By quantitative measurements on the poisoning action of oxygen or water vapor in ammonia synthesis on iron catalysts where the reversible equilibrium

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

* $= 0.10$ or $x =$ *circa* 2.25. Hence, since $x = \frac{\lambda}{RT}$, $\lambda = 2 \times 2.25 \times 273$.

is established, Almquist and Black [22] showed that in the most active preparations only one iron atom in 200 had catalytic activity.

If the fraction of the surface active for a given reaction is specific for that reason and if this fraction varies widely from one reaction to another, it is evident that one may expect progressive poisoning. This was realized by Vavon and Huson [23] with platinum and by Kubota and Hoshikawa [24] with nickel catalysts. With the latter in the three reactions (1) the hydrogenation of benzene (2) the hydrogenation of ethylene (3) the reduction of nitrocompounds, it was shown by progressive poisoning that only a small fraction of the nickel surface was active for (1), a greater fraction for (2) and probably the bulk of the nickel surface for (3). Rideal and Wright [25] assume three types of active surface on charcoal, Fe-C-N interfaces, Fe-C interfaces, Fe-N interfaces each with their own specific activities and separately sensitive to poisons. If a substance may decompose or react in two stages with one and the same catalyst, one of these stages only being sensitive to a particular poison, it should be possible to use such a material as a protective poison. This is the effect of water in the dehydrogenation of alcohol in presence of copper. The first stage yields acetaldehyde and hydrogen

$$C_2H_5OH = CH_3CHO + H_2.$$

The acetaldehyde formed may further decompose

$$CH_3CHO = CH_4 + CO$$

but water is a poison for this reaction. Hence, as was shown by Armstrong and Hilditch,[26] better yields of acetaldehyde are obtained from aqueous alcohol than from absolute alcohol.

The kinetics of reactions in the presence of poisons will be similar to those of reactions in which one of the reactants acts as a retarding agent, the retarding agent now being a material extraneous to the reaction. The temperature coefficient of poisoned reactions will obviously depend on the nature of the poison whether permanent or transitory. Permanent poisons will have no influence on the temperature coefficient since they have merely put a certain fraction of the surface definitely out of action. With transitory poisons a higher temperature coefficient than for the unpoisoned reaction will obtain, as the coefficient will include the influence of temperature on the desorption of the poison, leaving more free surface for reaction.

Promoters.—If the catalytic effect produced by a given substance in a reaction is materially enhanced by the addition of a small amount of substance, itself not markedly catalytic, the catalyst is said to have been promoted and the substance so employed is termed the promoter. The term is usually restricted to cases where the amount of substance so employed is small. With more or less equal amounts of two materials the product is normally called a mixed catalyst; if the non-catalytic material is in large excess, it is usually termed a catalyst support.

The phenomenon of promoter action was discovered during the technical development of catalytic processes of hydrogenation and ammonia synthesis.[27] It was a logical consequence of a research conducted by Baxter [28] at a very much earlier date, for a very different purpose, on the occlusive power of nickel and cobalt for hydrogen, when these metals were prepared by reduction of the oxide in hydrogen. Baxter found that cobalt of atomic weight purity occluded negligible amounts of hydrogen. When the ordinary minute quantities of impurities, e.g., silica, were present, marked amounts of gas were occluded, the metal product being less compact, sintering being prevented.

The quantitative examination of a few promoted catalysts has been made. Wyckoff and Crittenden [29] showed by X-ray studies that iron catalysts for ammonia synthesis were of a smaller crystal unit when promoted with K_2O-Al_2O_3 than when pure, the promoter effect being, in part at least, therefore an extension of surface. Russell and Taylor [30] showed, however, that, in the synthesis of methane over nickel, an extension of surface equal to 20 per cent produced a tenfold increase in reaction velocity. This indicated a qualitative improvement of the surface rather than a quantitative extension as the principal cause of the observed effect. Almquist and Black,[31] in their poisoning studies already cited, showed that whereas in ordinary iron only about one atom in 2,000 had ammonia synthetic activity, this ratio increased to one in 200 for the good promoted catalyst. They showed also that the surface capacity was varied. These evidences of enhanced activity at interfaces is further strengthened by a research of Hurst and Rideal [32] on copper promoted by palladium, in which the ratio of $CO : H_2$ burned on the surface varies with the extent of promotion. Also the data of Rideal and Wright,[33] already cited (*vide ante*) support this concept of interface activity. It was pointed out by Taylor that the increase of crystal faces, edges and corners would increase the unsaturated catalyst atoms and that the enhanced activity of such unsaturated atoms would explain the quantitative data. An extension of this same idea has been more recently developed. Since Volmer and his associates [34] have shown the two-dimensional motion of adsorbed gases it is possible that such motion of reactant molecules will bring them to interfaces between crystals at which reaction will occur. Schwab and Pietsch [35] provide a name for such catalysis. They propose to call it adlineation. It must not be forgotten, however, that the extent of surface active is specific for a given reaction and that, in many cases, the whole surface is active, in which event, reaction at lines of interface must be only a part of the whole. It is obvious, also, that the greater the fraction of the surface which normally has activity in a given reaction the less will be the advantage accruing from the employment of promoters. Promoters will be most advantageously employed in those reactions which are most difficult to achieve (i.e., lesser fraction of active surface) with the normal catalyst.

Extent of Active Surface and Pressure.—The extent of the surface which is operative in a given reaction is also determined by the pressure at which the process is conducted, and this in turn may affect the kinetics of the process. This possibility is definitely confirmed by some recent work of Donnelly and Hinshelwood,[36] who have shown that the kinetics of the hydrogen-oxygen reaction on platinum at atmospheric pressure differs essentially from the results of Langmuir at very low pressures. Donnelly and Hinshelwood interpret these differences on the basis of the theory that the catalytic surface possesses centers of varying activity. At low pressures the amount of gas may be small enough to be accommodated on the most active centers, which, in virtue of their activity, are more likely to be susceptible to poisons, and may even be poisoned by too large a pressure of the reacting gases. At higher pressures, where the total adsorption is much greater, the less active centers, being much more numerous, contribute the greater proportion of the total reaction.

The experience gained in the study of catalysts as to the heterogeneous nature of the surface should have an influence on the general field of colloid chemistry. Many of the properties of the colloid particle are attributable to the unsaturation of surface atoms. In this direction lies a profitable field for intensive study and investigation.

Activated Adsorption at Reaction Surfaces.—Quite recently,[87] a hitherto unnoticed characteristic of adsorption processes involved in surface reactions has been demonstrated. It has been shown that adsorptions leading to surface reactions may be slow processes requiring a definite energy of activation characteristic of the adsorbent and the adsorbate. A general theory of such adsorption processes has been developed and it has been shown that the experimental consequences of such a theory have also been exhibited in earlier experimental studies of adsorption. To exhibit the relation between slow adsorptions having activation energy and specific processes at surfaces, we shall discuss data accumulated recently in this laboratory involving slow adsorptions of hydrogen on oxide surfaces which promote either dehydrogenation or dehydration processes.

The best experimental data demonstrative of the existence of two types of adsorption of hydrogen, one involving van der Waals' adsorption occurring rapidly with low activation energy, the other with relatively high activation energies and involving a definite activation of the adsorbed molecule, have been accumulated recently by A. T. Williamson and the writer in Princeton.[88] We have operated with two surfaces, one of manganous oxide, the other a mixture of manganous and chromium oxides having a higher specific activity. At both surfaces, the reaction occurring, for example with ethyl alcohol, is predominantly one of dehydrogenation. At —78° C., the hydrogen adsorption on a given sample of manganous-chromium oxide is small, rapidly attained and practically reversible by evacuation at the same temperature. At 0° C., the adsorption of hydrogen of this type is less than at —78° C., but there sets in an extremely slow adsorption, the rate of which only makes measurable changes in adsorption over periods of days. At 100° C. and 132° C., where the low-temperature, van der Waals' adsorption has fallen to negligible proportions, the rate of this second, activated adsorption has now risen to conveniently measurable velocities, and, for such measurements, activation energies have been calculated. The velocity of this activated adsorption increases rapidly with temperature. At 184° C. and 305° C., *the amount of adsorbed hydrogen has risen to fifteenfold that obtaining under similar pressure conditions at —78° C.* At 444° C., the extent of adsorption is still several times that at —78° C., but definitely less than at 305° C. under the same pressure. The adsorption is a real adsorption phenomenon, completely reversible, all of the hydrogen being recoverable as such by evacuation, requiring, however, continued pumping for long intervals of time at temperatures around 460° C. There is no evidence of water formation.

From the velocities of adsorption at 100° and 132° C., the activation energy of the adsorption process may be calculated by means of the equation $d\ln\frac{v}{dT}=\frac{E}{RT^2}$. In this way we have found the following values for the areas covered by the adsorption, respectively, of 0–10, 10–15, 15–20 and 20–25 $cm.^3$ The successive E values are 5920, 9500, 10500 and 10500 calories per mol adsorbed. Thus, with increasing surface covered, the velocity of adsorption sinks as the activation energy rises. The heats of adsorption calculated from the isosteres in the two temperature ranges exhibit most definitely the distinction between the two types of adsorption involved. In the range —78° to 0° C., the 7 $cm.^3$ isostere yields a value for the heat of adsorption of 1900 calories per mol. From the 305° and 445° C. isotherms, the isosteres yield a value for the heat of activated adsorption greater than 19,000 calories per mol. These divergencies in the heat data serve also to account for the sharp

increase in amount adsorbed in the two ranges of temperature. With the less active surface, manganous oxide, the data are of the same qualitative nature but quantitatively different. The energy of activation of the activated adsorption is higher ($\sim$ 10,000 calories per mol) even on the most active areas so that the velocity of this adsorption only becomes measurable at 184° C. The adsorptions per gram are also one order lower in magnitude.

The variation in the velocity of activating adsorption (and therefore also of desorption) with variation of the surface may be one of the important factors in determining the direction of reaction along a particular path. We may discuss this with reference to the alternative dehydrogenation and dehydration processes of alcohols at oxide surfaces. The final steps in these two reaction processes must consist in the recombination of the respective atoms or radicals at the surface and the evaporation of hydrogen or water molecules. These final stages are the initial stages in the activated adsorption of hydrogen or water if the activation involved in such adsorption consists in a dissociation of the molecule. On this view, activity in dehydrogenation at a given temperature should be associable with an activated adsorption of hydrogen at a somewhat lower temperature since desorption will occur more slowly than the adsorption and hence, for a given velocity, require a higher temperature. The hydrogen activation already recorded in previous paragraphs on manganous oxide surfaces is such that it would permit dehydrogenation processes to occur fairly readily in the temperature range about 300° C. This is in accord with the known activity of such oxides. On the other hand, with surfaces such as alumina, active almost exclusively as dehydration agents in the temperature range 200–300° C., it is obvious that, from the point of view here developed, there should be no activating adsorption of hydrogen gas.

This conclusion has been experimentally confirmed with an active dehydrating surface of alumina prepared by precipitation of the hydroxide by ammonia from aluminium nitrate and ignition at 400° C. The sample showed no measurable adsorption of hydrogen below 400° C. At 445° C. a slow measurable adsorption of hydrogen occurred and its velocity could be measured. The velocity of adsorption was considerably increased by raising the temperature to 525° C. In the temperature range from 445° to 525° C., the velocity of adsorption increases sevenfold. From these figures it is calculated that the activation energy of the process is of the order of 27,500 calories per mol adsorbed.

The adsorption was a reversible process, the hydrogen being evolved and removable by evacuation at a higher temperature. No water was formed by reduction of the oxide. It is apparent, therefore, from such experiments, that dehydrogenation cannot occur in the temperature range of dehydration (200–300° C.) because of the slowness with which such surfaces at such temperatures effect the activation of hydrogen or the reverse recombination of hydrogen atoms. An activated adsorption of water vapor in this same temperature region at a sufficiently rapid velocity would suffice therefore to account for the predominant dehydration activity of alumina under such conditions. An experimental study with water vapor analogous to those discussed above for hydrogen is now in progress.

Some parallel experiments by Alyea [39] on powdered pyrex glass confirm the point of view here presented. Alyea has shown that the adsorption of hydrogen on powdered pyrex glass increases from immeasurably small values in the low temperature range to large values ($\sim$ 6 cm.^{3} per 100 grams at low gas pressures) in the temperature range 480–520° C. This adsorption of hydrogen by glass has been associated by Alyea with the known influence of

surface on the explosive reaction of hydrogen and oxygen. The high temperature range in which the activated adsorption of the hydrogen occurs is also consistent with the predominantly dehydration characteristics of glass and silica surfaces in a lower temperature interval.

What has been thus outlined for the specific cases of dehydrogenation and dehydration may be adapted to other types of reaction and may serve as a useful method of approach to the whole field of specific surface activity. Thus, the nature of the association between the hydrogen halides and various halide surfaces is doubtless fundamental to the problem of addition of hydrogen halides to unsaturated organic compounds. Furthermore, it is obvious that the necessary activation need not be limited to the one reaction species. On certain surfaces and for certain reactions both reactants may require activation. There is some evidence in the recent work of Elgin [40] on the hydrogenation of different types of sulfur compounds on metallic surfaces that the most resistant sulfur compounds, such as thiophene, require the most active fractions of the reaction surface for surface activation.

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Adsorption by Silica Gel, Theory and Applications

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Theory.

The adsorption of gases and vapors by certain porous bodies such as charcoal, kieselguhr, etc., has long been a matter of common knowledge. It was soon found that the retention of gases and vapors by such adsorbents was not related to the chemical composition of the substance adsorbed, but was in some way connected with the ease of condensation of the adsorbed gas or vapor. A rough parallelism was noted between the adsorption of a gas and the boiling point of the gas when condensed to a liquid.

Much of the uncertainty and inaccuracy of the early adsorption work was due to the difficulty of preparing adsorbents of constant properties. When it was found that adsorbents could be prepared from certain colloidal solutions in an easily reproducible manner, it then became possible to study the phenomenon of adsorption with some degree of certainty. Furthermore, when it was found that these latter adsorbents possessed the power of adsorption equal, if not superior, to that exhibited by adsorbent charcoal, the experimental study was made comparatively simple.

Silica gel, prepared from the coagulation of a colloidal solution of silicic acid, is such an adsorbent, and in many respects is an ideal substance for the study of adsorption. It is easily made under conditions that may be reproduced with considerable exactness. It is prepared from inexpensive raw materials which are available in unlimited quantities. Chemically, it is most inert and is, therefore, stable in air, even at high temperatures.

The word "gel" does not accurately suggest its physical nature, but rather indicates its condition at one stage of its manufacture. As actually used, it is a hard, glassy material, with the appearance of a clear quartz sand, and of the chemical formula SiO_2. The thing that differentiates it from ordinary sand, however, is its highly porous structure, and especially the size and uniform arrangement of these pores.

The adsorption of a number of gases by silica gel has been studied at different temperatures. From the results of such experiments it has been possible to discover the factors that are of importance in determining the extent of adsorption.

It was found that vapors of liquids of a high boiling point were more strongly adsorbed than vapors from a liquid of a low boiling point. Furthermore, adsorption decreased with increasing temperatures. Also, the greater the partial pressure of vapor being adsorbed, the greater was the extent of the adsorption. All these facts suggested the idea of condensation of the vapor in the adsorbent. Pursuing this thought we selected as a measure of the ease of condensation the ratio of the pressure of the vapor in equilibrium with

the adsorbent to the vapor pressure of the liquid at the temperature of adsorption. This ratio is herein designated as the "corresponding" pressure. It was soon established that vapors of high corresponding pressure were more strongly adsorbed than those of lower corresponding pressure. The relationship, while qualitatively true, did not correctly represent the phenomena quantitatively.

It was then noted that when the corresponding pressure equaled unity, i.e., when adsorption was measured at the vapor pressure of the liquid, the volumes of the adsorbed liquid were in all cases the same. In other words, it is advantageous, inasmuch as it tends towards simplicity, to express adsorption in terms of volume of adsorbed liquid rather than in weight. The volume of adsorbed liquid was obtained by dividing the weight of the substance adsorbed by the density of the liquid at the temperature of adsorption.

This simple relationship was found to be true only in the case of measurements carried out at a corresponding pressure of unity. At lower corresponding pressures the volume of the adsorbed liquid was not the same at the same corresponding pressure. This discrepancy was attributed to the fact that the condensed liquid under corresponding pressures less than unity had a density smaller than the normal density. Furthermore, the greater the compressibility of the liquid the greater was the deviation of the density of the liquid in the adsorbent from the normal density. By taking these additional facts into consideration all experimental observations were quantitatively brought into complete harmony. It can therefore be said that the factors influencing adsorption are the corresponding pressure, and the compressibility of the adsorbed liquid.

We have yet to consider the properties of the adsorbent that determine its activity. Inasmuch as the chemical nature of the latter apparently is of no moment, we are forced again to a consideration of a physical property. All adsorbents are porous, and the internal volume is large and composed of exceedingly fine pores. Furthermore, capillarity tells us that a liquid in a small tube possesses a lower vapor pressure than the normal vapor pressure. In other words, it is easier to condense a vapor within a small capillary than on a level surface. We have, therefore, in the above all that is necessary to characterize an adsorbent. It must possess as large an internal volume as possible and this volume must be made up of spaces of minimum dimension.

When we consider silica gel as an adsorbent for the vapor of a liquid at a given temperature, we have to take into account two things: (1) the partial pressure or concentration of the vapor to be adsorbed; and (2) its vapor pressure at the temperature of adsorption. Denoting the partial pressure by P and the vapor pressure by P_0, we may definie the "corresponding pressure" by the quotient $\frac{P}{P_0}$. It has been found experimentally that the amount of a particular vapor adsorbed increases with increasing value of the ratio $\frac{P}{P_0}$. Now for a given partial pressure, the value of $\frac{P}{P_0}$ increases with decreasing temperature, and for a given temperature, the ratio $\frac{P}{P_0}$ increases with the increase of partial pressure. Hence in practice, we have better adsorption the lower the temperature and the greater the concentration of the vapor to be adsorbed. Maximum adsorption, at a given temperature, will take place when $\frac{P}{P_0}$ has its maximum value, which is unity.

Let us consider a few examples. We may adsorb water vapor at 30° C. from air saturated at 30° C. Under these conditions, $P = P_0 = 30$ mm., and the gel will take up an amount of water corresponding to 25 to 27 per cent of its own weight.

If we consider a similar mixture of sulfur dioxide and air at 30° C., that is, a mixture in which the partial pressure of sulfur dioxide is 30 mm. (which corresponds to about 4 per cent by volume), the ratio $\frac{P}{P_0}$ is much smaller than in the case of water, due to the greater vapor pressure of sulfur dioxide. From such a mixture the gel takes up sulfur dioxide to about 6 per cent of its own weight.

If we use a mixture of carbon dioxide and air of the same concentration as above, the value of $\frac{P}{P_0}$ at 30° C. is quite small and only a slight amount of carbon dioxide will be adsorbed. For the permanent gases the ratio at 30° C. is extremely small and hence in all the above cases the adsorption of air is negligible.

The effect of temperature is shown by the following: From a mixture of sulfur dioxide and air containing 4 per cent by volume of sulfur dioxide (partial pressure about 30 mm.), the gel takes up 4, 6, 8.2 and 11.1 per cent sulfur dioxide by weight at 40°, 30°, 20°, and 10° C., respectively. The effect of concentration may be illustrated by the following: Working at 30° C., the gel takes up 2.3, 6, 7.1 and 8 per cent by weight of sulfur dioxide from mixtures containing 1, 4 6 and 8 per cent, respectively.

Inasmuch as the adsorptive power of silica gel does not depend upon any specific chemical action, but rather upon the physical properties of the vapor to be adsorbed, it may be used successfully at ordinary temperatures and atmospheric pressure to remove from air the vapors of any liquid mixed with air in any proportions, provided the liquid boils, under atmospheric pressure, above —10° C. We must exclude, of course, any vapor which like hydrofluoric acid attacks silica.

From what has been said it will be obvious that lower boiling liquids may also be adsorbed, but it would hardly be practicable to do so efficiently at the ordinary temperature. Even the so-called permanent gases may be adsorbed at low temperatures, and it is quite likely that such a problem as the fractionation of liquid air into oxygen and nitrogen would be made easier by the use of silica gel.

From what was said above in the discussion of corresponding pressure the obvious procedure to follow in order to recover the adsorbed material consists in two steps: (1) raise the temperature, and (2) decrease the partial pressure of the vapor over the gel by evacuation or by displacement with air, steam or other vapor.

Thus adsorbed water may be driven out by air at 115° C., more rapidly at 125° C., and still more rapidly at 150° C. High boiling liquids may be adsorbed without difficulty, but require a correspondingly high temperature for recovery from the gel. Silica gel is almost ideally adapted to the adsorption and recovery of the vapors of liquids boiling between 30° and 150° C. in that it takes up large quantities of these vapors at room temperature and gives them up readily at slightly elevated temperatures, that is, from 100° to 200° C. This classification includes most of the important solvents, such as ether, acetone, methyl and ethyl alcohol, benzene, gasoline, methyl and ethyl acetates, and many others. We shall see also that it offers a satisfactory

means for drying air and for the recovery and concentration of the vapors of more volatile liquids such as sulfur dioxide.

As a corollary to what happens physically in the pores of a gel to bring about such a remarkable reduction of vapor pressure, the following theory is advanced as an explanation of this most interesting phenomenon.

On Figure 1, two tubes of widely different diameter are shown. *"A,"* on the left, represents a tube 10 cm. in diameter (or it may be any other diameter of that magnitude). It is partly filled with liquid. At the walls of the tube, will be noted the familiar meniscus, where the liquid climbs slightly above the level of the liquid in the center of the tube. Observation will show that for some distance from the center of the tube, the liquid surface is practically flat. Now draw on your imagination when you look at *"B,"* since in this case, we are trying to come to close quarters with molecules, and picture the inside of one of the pores of silica gel as having a diameter of 4×10^{-7} cm. The surface of the liquid is now curved from wall to wall, thus forming a continuous arch of molecules, tangent to each other and held firmly in position by their mutual attraction.

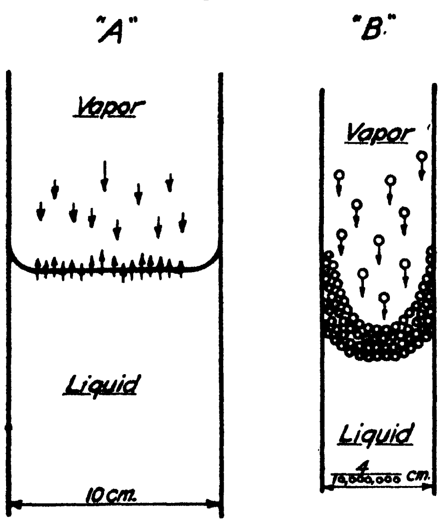


FIG. 1.

Referring again to *"A,"* and keeping in mind that this tube is 10 cm. in diameter, practically no reduction in the vapor pressure of the liquid contained therein can be observed. This is due to the fact that through the flat portion of the liquid surface, there is an unrestricted flow of molecules to and from the vapor space above the liquid. This free interchange of molecules tends to establish a pressure in the space over the liquid, equal to the normal vapor pressure of the liquid itself.

Turning again to *"B"* it will be noted how the molecules at the liquid surface are arranged in a complete curve from wall to wall. This suggests the possibility that such a barrier could effectively prevent the escape of molecules from the liquid to the vapor space above. Upon this hypothesis, it can readily be seen, that if we remove all air from the gel, it is possible to have in the pores of the gel an almost perfect vacuum, even though the pores themselves are partly filled with a volatile liquid. This reduced pressure persists until the pores are filled with liquefied vapor.

Silica gel is made from two very well-known chemical materials, sodium silicate and sulfuric acid, the former being commonly known in the trade as water glass. The real difficulty of making silica gel commercially was to find how to mix the two materials so they would make a good gel. If you mix them in any other but the exact way, they will not make a gel, but a precipitate, which has no gel qualities whatever, though it may analyze, chemically, exactly the same and have the same appearance.

After the proper mixing and allowing this mixture, identified as the hydrosol, to coagulate into a hydrogel state, it is necessary to subject the hydrogel to a very thorough washing to eliminate all the products of reaction, principally sodium sulfate, which is not easy to remove. This hydrogel must

be dried very carefully, after being purified, so as not to break it into two small pieces. It must be remembered that the hydrogel consists of approximately 90 per cent water and 10 per cent silica. We must, therefore, eliminate nine parts of water, in order to have one part of silica left as the final product, viz., silica gel.

The gel itself is a porous body, its internal volume being about 50 per cent of its total volume. We do not know exactly what it looks like on the inside. The configuration of the pores we are unable to study. They are too small to be seen by any optical means, since the dimensions are actually below the wave length of light. We have, however, two conceptions of what the interior might look like if one could see it. First, we picture it as being simply a body of spherical particles of sub-microscopic size piled together, much as you would pile cannon balls. A second conception would be that of a shredded wheat biscuit, except it is much more symmetrical and the shreds intermesh with one another at all conceivable angles. It is impossible to measure directly the size of the pores.

Physical chemists tell us, however, that if we fill a capillary tube with a given liquid, the vapor pressure of the liquid is reduced, and the smaller the diameter of the tube, the greater is the reduction of the pressure. Calculations have been made to determine the average diameter of the pores in silica gel, based on the observed effect gel has on the vapor pressure of a given liquid, and a diameter of 4×10^{-7} cm. has been arrived at by this method. We know the molecules of most substances have a diameter of about 3×10^{-8} cm., so that the pores of silica gel are roughly ten times as large in diameter as the average molecule. A further discussion in detail of the theory of adsorption as applying to sulfur dioxide may be found in an article by W. A. Patrick and John McGavack, Jr., which appeared in the May, 1920, issue of Journal of the American Chemical Society.

Adsorption by silica gel embraces two general classifications, namely, adsorption in the vapor phase and adsorption in the liquid phase.

Vapor Phase Adsorption.

The following data and description pertain to experimental results, obtained on a laboratory scale, on the adsorption and recovery of the vapors of five typical substances, viz.: sulfur dioxide (b.p. —8° C.), ethyl ether (b.p. +35° C.), acetone (b.p. +56° C.), benzene (b.p. +80° C.), water (b.p. +100° C.). These will be considered in the order named.

The adsorption of sulfur dioxide by silica gel has been thoroughly studied both by the static and dynamic methods. The static method consists in placing a convenient amount of the gel in a small apparatus which is then exhausted to the highest vacuum obtainable. To insure complete removal of air the vessel is heated to 300° C., and this temperature maintained, with the pump in continuous operation, for six hours, or until no more air can be pumped off. The pump used is the Gaeda high vacuum mercury pump. The vessel containing gel is then placed in a thermostat and a known amount of sulfur dioxide introduced. After the system has come to equilibrium, which requires not over fifteen minutes, the pressure is observed and the quantity of sulfur dioxide adsorbed determined. Figure 2 gives the results of four series of results obtained in this way at 0°, 30°, 40° and 100° C., respectively. Figure 3 gives a recalculation of these results in which the ordinates express the adsorbed sulfur dioxide as per cent of gel weight, instead of cc. per gram of gel.

The dynamic method consists in placing a convenient quantity of granular gel, usually 10 grams, in a glass tube of 1 to 2 sq. cm. in section, bent in the form of a U for convenience of immersion in the thermostat, and passing through the gel at a given temperature a definite mixture of sulfur dioxide and air. The air and sulfur dioxide are metered separately through carefully calibrated flow meters similar to those used by the Chemical Warfare Service, passing first into a mixing chamber and thence over the gel. Under these conditions the gel adsorbs the sulfur dioxide completely for a certain period. At the end of this period a trace of gas begins to come through, the percentage of sulfur dioxide in the exit gas increasing rapidly, becoming finally equal to that of the entering gas. This corresponds to the point of saturation for this particular mixture and temperature.

The results of a series of experiments in which the concentration of the sulfur dioxide air mixture varied from 0.5 to 8 per cent by volume and the temperature varied from 10° to 40° C. are given in Figure 4. A comparison of Figures 3 and 4 shows substantial agreement between the results given by the two methods. In other words, the presence of a permanent gas has, for practical purposes, a negligible effect upon the adsorption of sulfur dioxide by silica gel.

The details of one set of experiments (at 20° C.) are shown in Figure 5, in which the results are shown as percentage efficiencies against time. The ordinates here express the sulfur dioxide adsorbed as percentage of the total being admitted to the gel. With regard to these experiments we desire to make the following comments:

1. The rate of flow of gas through the gel was 40 cc. per minute per gram of gel or 0.65 cubic foot per minute per pound of gel. This means that the time of contact of gas with gel was approximately 0.8 second.

2. Notwithstanding this short interval allowed for adsorption, in each run no detectable trace of sulfur dioxide passed the gel for a considerable period. In other words, we had 100 per cent adsorption for a certain period, depending upon the concentration, after which the efficiency curve fell off abruptly to zero adsorption. We denote the time at which the first trace of sulfur dioxide comes through as the "break-point." An examination of the curves at 20° C. will show that for all concentration the gel was not less than 57 per cent saturated at the break-point.

3. As already stated the rate used in these experiments was 40 cc. per minute per gram of gel, which allows about 0.8 second for contact. If necessary, higher rates may be employed.

Reference to Figure 6 shows that for a 0.75 per cent gas the slopes of the efficiency curves are very nearly the same for rates ranging from 25 cc. to 75 cc. per minute per gram of gel. A practical rate for adsorption in general is 50 cc. per minute per gram of gel, which is approximately 0.8 cubic foot per minute per pound of gel. This allows about 0.6 second for contact.

The gel granules used in all these experiments varied in size between 8 and 14 mesh. The size of the gel particles has a very practical bearing in two respects. In the first place it is obvious that the larger the particles the greater the time necessary for the adsorbed material to penetrate to the interior and that, for adsorption purposes, it would be desirable to reduce the size of particles as much as practicable. The final saturation value would not be changed, but the break-point would occur later and the latter part of the efficiency curve would be steeper, which is advantageous.

With respect to the recovery of adsorbed material, silica gel has marked advantages over other adsorbents. By reference to the curves already given it will be seen that the gel takes up very little sulfur dioxide at 100° C., even with high concentration of gas. These curves indicate the obvious procedure

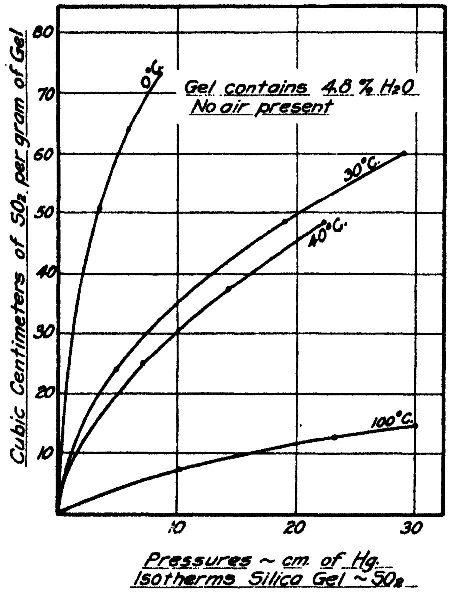


FIG. 2.

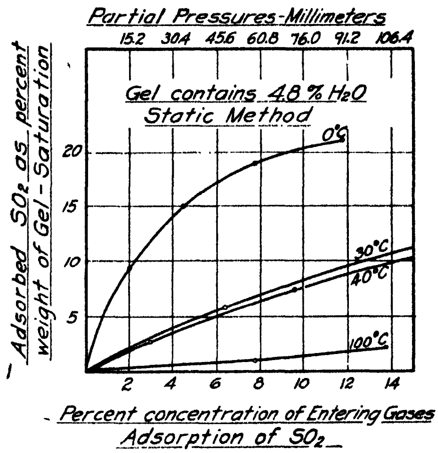


FIG. 3.

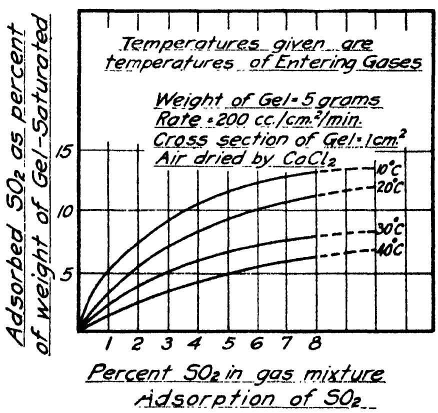


FIG. 4.

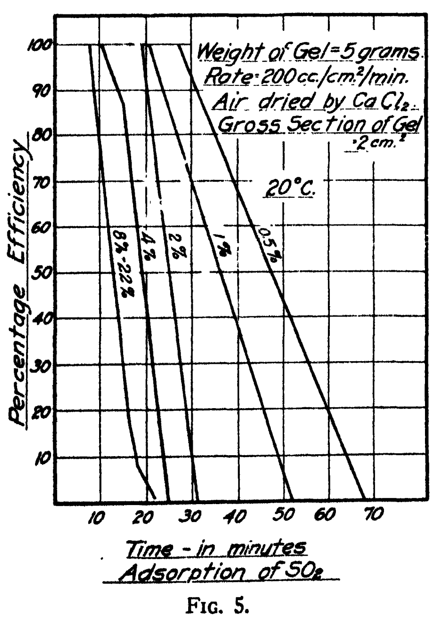


FIG. 5.

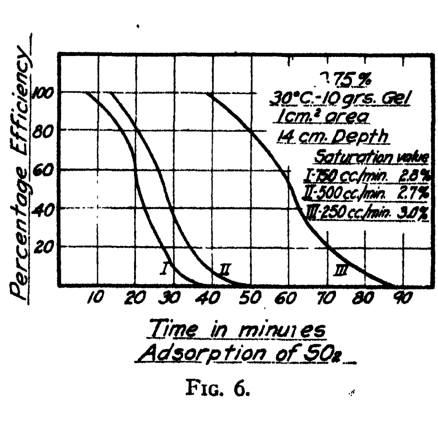


FIG. 6.

to follow in using the gel. Adsorption should take place at as low a temperature as is practical and for recovery the whole should be heated to 100° C. or more. The exact procedure to be used depends upon the concentration of sulfur dioxide desired.

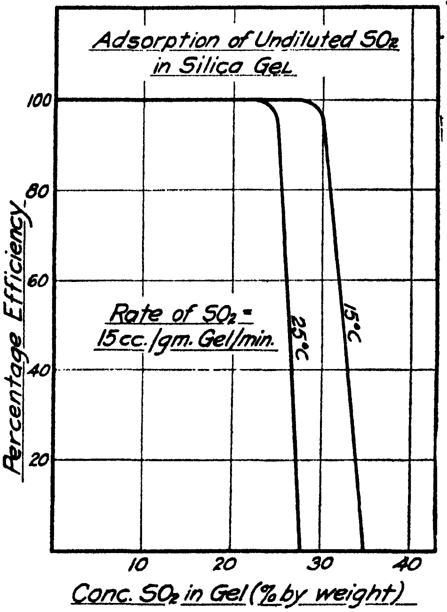


FIG. 7.

Let us assume for example that we have a gas which is 4 per cent sulfur dioxide by volume, and that we wish to concentrate this to 8 per cent for use in the lead chamber process for making sulfuric acid. And let us assume an adsorption temperature of 30° C. We see from the curves that using a 4 per cent gas and working at this temperature, the gel will take up 6 per cent of its own weight of sulfur dioxide. After adsorption the temperature is raised to 100° C. and the sulfur dioxide swept out by means of an air stream, the volume of air being so regulated to give the desired concentration. We may, if it is so desired, obtain in this way a much higher concentration than 8 per cent. It is possible to go from 4 per cent to 30 per cent in one step by simple air displacement at atmospheric pressure. It is easily possible in this way to concentrate as lean a gas as 1 per cent to 8 per cent in one step.

If the object is to obtain a very high percentage gas, as for example in making liquid sulfur dioxide, air would not be used, but the adsorbed gas liberated at 100° C. or above, by evacuation. By proper regulation of temperature, pressure and volume of air admitted, any desired concentration up to practically 100 per cent may be obtained.

Figure 7 shows the adsorption curves of silica gel for pure SO_2 at atmospheric pressure and temperatures of 15° and 25° C.

RECOVERY OF SOLVENT VAPORS.

Considerable losses of valuable solvents such as ether, acetone, alcohol, benzene, etc., occur in a variety of industrial processes. In the recovery of such solvents silica gel finds one of its most important applications. The general principles already discussed apply in this field and the adsorptive power of the gel for the vapor of a particular solvent can be predicted approximately before determining it experimentally. These general principles have already been illustrated in some detail by experimental data on sulfur dioxide.

For the recovery of solvents after they have been adsorbed by the gel, the most satisfactory method, applicable in nearly all cases, consists in heating the gel to the proper temperature and sending steam directly through it. For the volatile solvents here considered 105° C. is sufficient to bring about rapid distillation from the gel. This method is particularly adapted to the recovery of substances which, like ether, benzene, etc., are but slightly soluble in water and do not react chemically with it.

In reference to the percentage recoveries of the various solvents as shown in the following pages, it should be pointed out that, working on such a small scale, the experimental errors are relatively large. No particular effort was made to eliminate losses in handling and weighing the distillates.

The method of obtaining the solvent vapor-air mixture of the desired concentrations for the following adsorption tests was as follows:

A carefully metered volume of air, dried by passing through gel and phosphorous pentoxide, was passed through several bubbler bottles containing the pure solvent desired. The solvent bubbler was kept in a constant temperature bath. The mixture was passed through a weighed tube of silica gel, the solvent being adsorbed and the increase in weight noted. From these figures the additional volume of dry air to be mixed with the solvent air mixture was calculated to give the concentration desired. This final mixture was also carefully tested for concentration of solvent and then passed through a coil in a constant temperature bath and then through the gel to be tested, also in the bath. Weighings were made at regular intervals on the test gel and also on a trap tube of gel (in the case of water vapor P_2O_5).

In the following curves the term "break-point" means the percentage concentration of vapor in the dry weight of gel when the adsorption efficiency falls to 99 per cent. 100 grams of gel containing 4.5 per cent H_2O after activation is only 95.5 grams of dry gel. This weight is arbitrarily selected as the basis on which the concentration is always figured. The efficiency of adsorption usually is practically 100 per cent to within 0.5 per cent of the 99.0 per cent break-point. The term "saturation" means the percentage concentration of vapor in the gel by weight (dry basis) when the partial pressure of the vapor in the effluent air is identical with that in the inlet air; in other words, when the adsorption efficiency is zero.

Details of the standard laboratory set-up and instructions as followed in the laboratories of The Silica Gel Corporation are shown in the following illustration, Figure 8.

Ethyl Ether. Very little study has been made of the adsorption of ether from air mixtures as such, inasmuch as ether usually is found mixed with other organic solvents as well as water vapor in industrial plants. Practically all tests on the adsorption of solvents with silica gel have been made on air mixtures containing two or more solvents in the vapor form.

A 1.5 per cent by volume ether-air mixture or approximately 0.5 gallon of ether per 1,000 cubic feet at a temperature of 25° C. was passed through activated silica gel at a rate of flow of 50 cc. per gram of gel per minute. This showed a concentration of 11.2 per cent in the gel by weight at the 99 per cent efficiency break-point and a final saturation value of 17.8 per cent in the gel by weight at the temperature mentioned.

Two recovery experiments were carried out under slightly different conditions.

Experiment 1.—100 grams of gel containing 29 grams of ether adsorbed from a saturated air mixture, temperature of condenser 20° C., temperature of receiver 0° C., receiver vented to air.

	Distillate		
	Ether		Water
	Grams	Per Cent of Total	Grams
During heating to 107° C.	10.209	35.2	none
15 minutes of steaming	14.376	49.5	0.755
20 minutes of steaming	none	none	....
Recovery	24.585	84.7	....

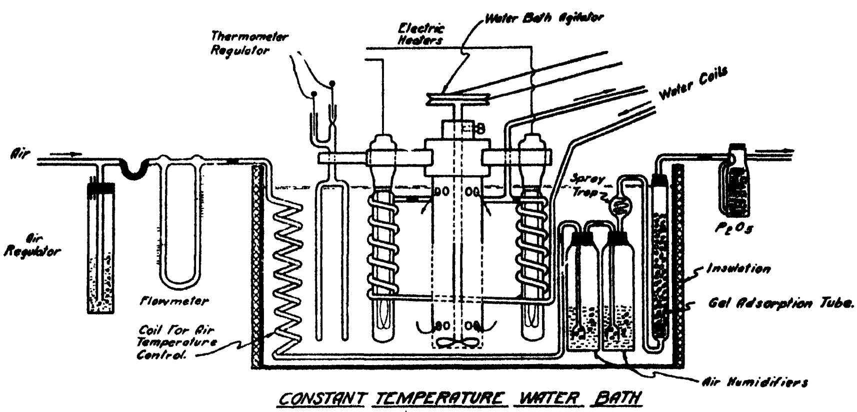


FIG. 8.—Standard Method and Equipment for Testing Granular Silica Gel for Adsorption of Water Vapor or Other Volatile Liquids at Specific Temperatures.

1. Reduce moisture content of gel to about 4% by heating in an electric oven to 600°-650° F. for 2-3 hours.
2. Tube for gel should be approximately one sq. cm. in cross-section and hold from 6 to 8 grams of gel.
3. Pass atmospheric air saturated at 25° C. at rate of 50 cc. per gram of gel (dry basis) per minute (equivalent to about 10 grains of moisture per cu. ft.) through the gel in tube as shown below.
4. Weigh gel and P_2O_5 tubes at regular intervals of about 30 minutes.
5. Increase in gel weight divided by sum of increase in gel and P_2O_5 weight gives the per cent efficiency of adsorption by the gel. This efficiency of adsorption *at any concentration* is shown by plotting the per cent efficiency of adsorption against per cent concentration in gel (dry basis).
6. A curve showing the *average efficiency* of the gel *up to any particular concentration* can be drawn by plotting the progressively averaged per cent efficiency of adsorption against the per cent of concentration.

$$m = \%\ \text{volatile matter in gel}$$

$$\%\ \text{dry basis} = \frac{m}{100-m}$$

At the end of the experiment, no ether was left in the gel. The 15.3 per cent loss was principally due to evaporation through the vent in the receiver and to experimental losses in handling and weighing. The next experiment used colder water in the condenser in order to minimize the loss by evaporation through the vent in the receiver.

Experiment 2.—100 grams of gel containing 30.5 grams of ether adsorbed from a saturated air mixture, temperature of condenser 0° C., temperature of receiver 0° C., receiver vented through a tube containing silica gel.

	Distillate		
	Ether		Water
	Grams	Per Cent of Total	Grams
During heating to 107° C.	9.769	32.	.....
10 minutes of steaming	17.821	58.4	17.545
20 minutes of steaming	none	....	.....
Recovery	27.590	90.4	.....

The vent tube adsorbed 0.095 gram of ether.

Acetone. Figure 9 shows the results of several experiments on the adsorption of acetone vapor at 25° C. from mixtures with air.

The results of three experiments in the recovery of adsorbed acetone follow:

Experiment 1.—A tube containing 100 grams of gel with 33.8 grams of acetone adsorbed from a saturated air mixture was connected with a source of steam, a condenser and a

receiver as previously described. During the heating some acetone was distilled out and condensed in the receiver but the amount was not determined separately. When the temperature reached 105° C., steam preheated to 112° C. was passed through the gel for a period of 80 minutes and 94.44 cc. of condensate was obtained which had a density of 0.94094. This corresponds to 33.77 grams of acetone or 100 per cent recovery.

Experiment 2.—100 grams of gel containing 33.3 grains of acetone adsorbed from a saturated air mixture, temperature of condenser 20° C., temperature of receiver 0° C., receiver vented to air. During heating to 107° C. 8.0485 grams of acetone distilled over. Steam was then passed for 20 minutes, giving a distillate of 16.9726 grams, having a density of 0.81529 at 25° C. This corresponds to 15.36 grams of acetone and 1.6126 grams of water. Further steaming for 30 minutes gave a distillate of 26.69 grams, having a density of 0.9770 at 25° C. This corresponds to 3.87 grams of acetone and 22.82 grams of water. Acetone recovered was 27.28 grams or 82 per cent of the total.

Experiment 3.—100 grams of gel containing 33 grams of acetone adsorbed from a saturated air mixture, temperature of condenser 0° C., temperature of receiver 0° C. 6.062 grams of acetone distilled over during heating to 107° C. and steaming for 10 minutes gave 34.47 grams of distillate having a density of 0.8654 at 25° C. This corresponds to 24.8184 grams of acetone and 9.6516 grams of water. Further steaming gave no liquid acetone. Acetone recovered, 30.8827 grams or 93.5 per cent of the total. During distillation the receiver was vented through a column of gel. Only a negligible increase in weight occurred.

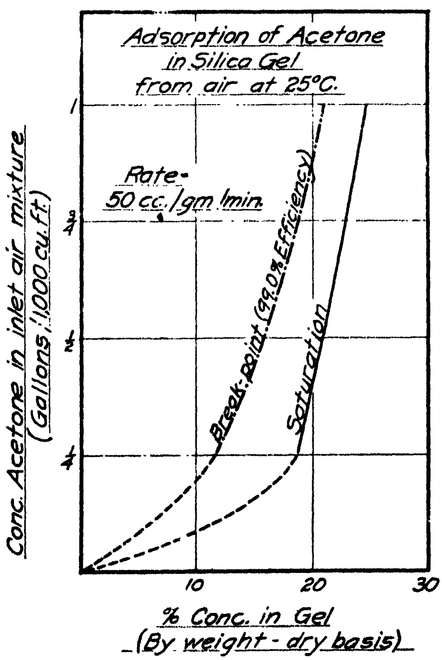


FIG. 9.

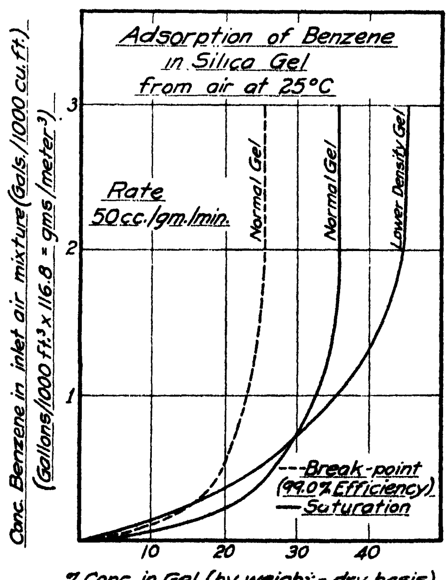


FIG. 10.

Benzene. Figure 10 shows the results of some adsorption tests on benzene (benzol) at 25° C. The gel used for the curves designated "normal gel" is similar to that used in the adsorption experiments with the other vapors described herein. The gel used for saturation curve designated "lower density gel" is, as the name suggests, a gel of somewhat lower apparent density. No break-point curve is included for the lower density gel as the efficiency was below 99 per cent up to the break-point.

It might be noted here that "high density" or small pore gel, although having a smaller capacity than "low density" or wide pore gel, holds the vapor more tenaciously and reduces the partial pressure of the vapor to a greater extent. Therefore, for the highest adsorption efficiency the "high density" gel is the better. This is particularly true in industrial solvent recovery work where the concentration of solvent vapor in the air mixture is low, usually one gallon or less per 1,000 cubic feet. It can be seen from the curves in Figure 10 that when the inlet concentration of solvent decreases to three-quarters of a gallon per 1,000 cubic feet the saturation value of the "high density" gel becomes almost identical with that of the "low density" gel, showing that the former is much better as an adsorbent on low inlet concentrations.

By controlling manufacture so as to make a gel of very low apparent density a saturation value even greater than that shown by the "lower density gel" in Figure 10 can be obtained. Such a gel, although having a large capacity and showing high concentration of solvent at saturation, when used for adsorbing vapor from a high concentration inlet mixture, is of no value for industrial solvent adsorption work, where the concentration of solvent in the air mixture is always very low.

Two experiments on benzene recovery are given, differing with respect to the temperature of the condenser and the amounts of adsorbed benzene present.

Experiment 1.—100 grams of gel containing 21 grams of benzene, temperature of condenser 20° C., temperature of receiver 0° C., receiver vented to air.

	Distillation Benzene Grams	Distillation Benzene Per Cent of Total	Water Grams
During heating to 107° C.	none	....	none
20 minutes of steaming	17.6282	83.9	4.1755
45 minutes of steaming	0.5489	2.6	51.5
Recovery	18.177	86.5	......

Experiment 2.—100 grams of gel containing 33.5 grams of adsorbed benzene, temperature of condenser 0° C., temperature of receiver 0° C., receiver vented through gel.

	Distillation Benzene Grams	Distillation Benzene Per Cent of Total	Water Grams
During heating to 107° C.	none	....	none
10 minutes of steaming	30.9716	92.1	6.2852
30 minutes of steaming	1.1515	3.4	54.335
Recovery	32.123	95.5	......

We have seen that silica gel, even after activation, always contains some water. The water content varies between 4.5 and 7 per cent by weight, depending upon the temperature and time of activation. By prolonged heating in a hot air stream, the water content may be reduced below 4.5 per cent, but gel with 4.5 to 5 per cent water content gives better adsorption results.

Water. The adsorption curves given in Figure 11 were composited from a very large number of tests. It is to be noted that the inlet concentration of water vapor in the air was determined at 25° C. For the 40° and 50° C. curves the 25° C. air-vapor mixture was passed through a coil in a constant temperature bath so that the mixture entered the gel adsorption tube at the same temperature as the gel, namely, 40° and 50° C. respectively.

Figure 12 gives in graphic form a summary of a large number of experiments on the removal of adsorbed water by air displacement. Experiments have shown that at temperatures from 125° to 200° C., the rate of removal is dependent mainly on the volume of air used, and increases only slightly with increase in temperature. We accordingly do not include here work done above 125° C.

Curves I, II, III and IV show the percentages of adsorbed water removed against time for rates of air flow ranging from 5 cc. to 50 cc. of air per

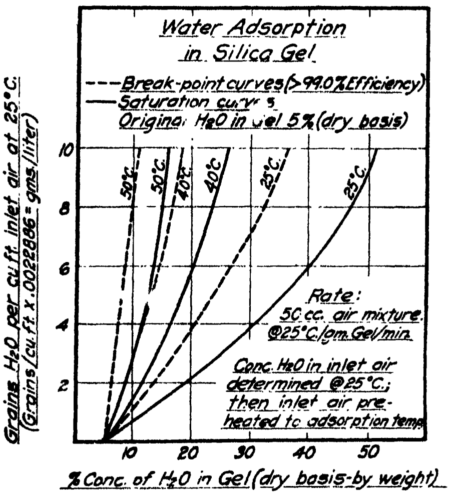


FIG. 11.

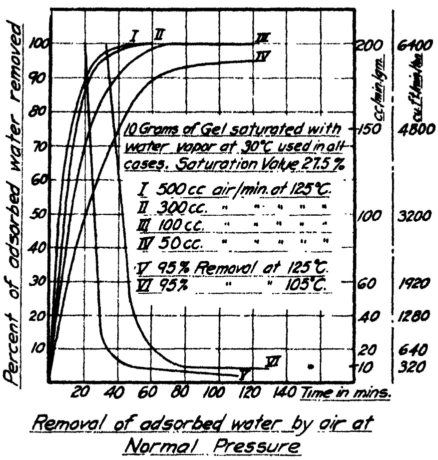


FIG. 12.

minute per gram of gel. An examination of curves III and IV indicates that the adsorbed water is removed about as rapidly with air at 30 cc. per minute as with 50 cc. per minute.

Curves V and VI show the same experimental results in which the rate of air flow is plotted against the time necessary to remove 95 per cent of the adsorbed water at 125° and 105° C. respectively. An inspection of these two curves will make clear that at these temperatures little will be gained by increasing the rate much above 20 or 30 cc. per minute per gram of gel.

Liquid Phase Adsorption.

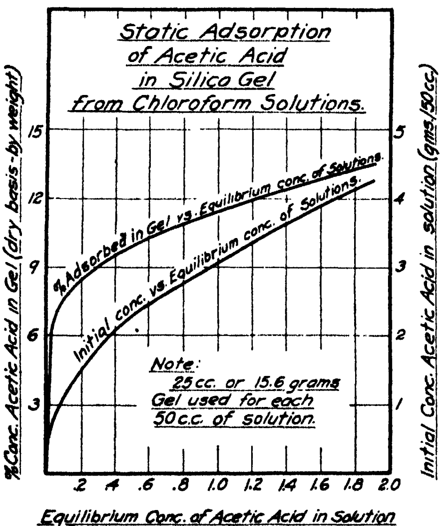
For the treating of liquids, it is essential that silica gel be pulverized to about 200 mesh, for otherwise the time required to reach maximum saturation with respect to the impurities being removed from a given distillate would be so great as to be prohibitive from a practical standpoint.

In nature we meet with a number of porous materials, such as fuller's earth, bauxite, kieselguhr, clays, etc., which, when properly activated, possess to a very limited extent an internal structure similar to silica gel. Since the exact dimensions of the pores of such materials absolutely fixes their adsorption power, it is not to be wondered at that in nature there has not been discovered any material of just the right physical structure to satisfy the exacting requirements of a highly adsorptive material adapted to commercial conditions.

The natural products mentioned all possess very marked ability to clarify liquids in which coloring matter is held in suspension. In this respect most

of them are superior to silica gel. It has been shown by extensive tests that when materials have pores so large as to permit the ready entrance of solid particles, these pores are too large to bring about the separation of two liquids that are in true solution. In silica gel, the preponderant proportion of the pores are of the proper size to effect the selective adsorption desired, but it nevertheless also has sufficient decolorizing properties to satisfy the strictest commercial demands in this respect.

It is obviously impossible that any material should at the same time have a structure possessing both maximum clarifying properties and maximum power to effect the separation of two liquids from true solution, since the one calls for pores of large dimensions, while the other is dependent on a structure with pores of minimum size. The ideal material for industrial use must possess both properties in the correct proportion to accomplish the desired removal of both coloring matter and objectionable solutes.



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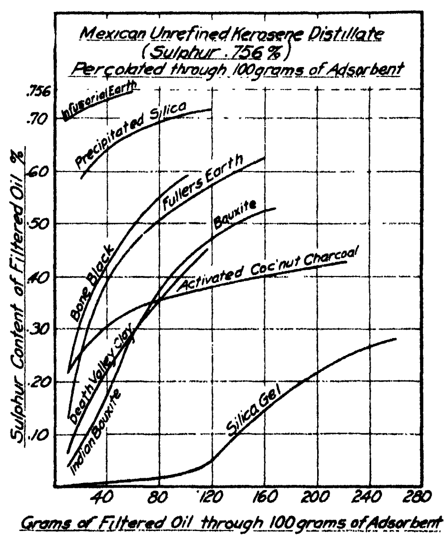

Fig. 14.

The curves in Figure 13 show the initial concentration of acetic acid and chloroform in solution and the percentage of acetic acid adsorbed by the gel from this solution. The curves were drawn from data compiled from a number of individual experiments with solutions containing various amounts of acetic acid, the initial and equilibrium concentrations of the acetic acid being determined in each case.

The curves plotted in Figure 14 show the relative ability of various commercial adsorbents to remove sulfur compounds from a Mexican crude kerosene distillate. An examination of this data discloses the fact that none of the other materials even approximates the capacity exhibited by silica gel. In fact, the quantity of any other adsorbent required to reduce the sulfur content of this kerosene to commercial requirements is so great as to preclude its use for this purpose.

For instance, if we attempt to use bauxite to make a finished kerosene containing 0.06 per cent sulfur from a crude kerosene containing 0.756 per cent sulfur, we obtain only fifteen parts of such an oil from one hundred parts

of bauxite. There would be left in the bauxite approximately 56 parts of oil higher in sulfur than the original crude kerosene, which would constitute so great a shrinkage in the amount of finished kerosene obtained as absolutely to forbid commercially such a procedure.

Silica Gel as a Catalyst.

It is doubtful if silica gel *per se* possesses any catalytic qualities such as are shown by iron gel, stannic gel, tungstic gel, vanadium gel, copper gel, etc., or combinations of these oxides known as plural gels. Results with silica gel tending to show catalytic reactions are due no doubt to some trace of impurities in the washing water, such as iron, which is difficult to remove economically. In organic reactions which require large reaction surfaces and also those reactions where dehydration occurs or water is formed as one of the products of reaction, e.g., $ROH + RCOOH \rightleftarrows RCOOR + H_2O$, it is quite likely that silica gel itself functions as the catalyst.

Silica gel as a carrier for catalysts is ideal, due to its porous structure and enormous surface area. Its surfaces can readily be impregnated with any of the metals or metal oxides in such concentrations and combinations as desired.

Probably the most important application of silica gel so far developed commercially is in the so-called contact sulfuric acid process. As a carrier for platinum it is ideal. It is chemically inert to sulfuric acid at high temperatures, stands up under continuous high temperature conditions, is resistant to mechanical action and offers an enormous surface upon which to distribute the platinum. Besides possessing these qualities silica gel mass has also proven insensitive to the usual negative effect of arsenic poisoning.

The gel mass is placed on beds of quartz covering the supporting trays in the converter. Broken quartz may also be placed on top of the gel beds to cause uniform dissemination of the SO_2 gas passing downward through the converter. In the event that the mass becomes contaminated with impurities of a combustible nature it is only necessary to pass air heated in the preheater, to about 800° F. through the converters for approximately 24 hours in order to eliminate the contamination. No removal of the mass is necessary.

The weight of platinum required per ton of SO_2 per day when using such carriers as magnesium sulfate or asbestos varies greatly in practice. The modern plant using these carriers requires less platinum than formerly. With silica gel only from 20 per cent to 25 per cent as much platinum is required to secure the same or better conversion, other plant conditions being the same for both types of mass. Ordinarily, it requires 100 pounds of silica gel per ton of 100 per cent H_2SO_4 per 24 hours to charge a converter, the platinum content being 0.125 per cent by weight.

With converters having proper temperature controls and a plant in which the SO_2 gas is properly cleaned and purified, conversions of 96 per cent can readily be obtained under normal operating conditions. *See* Figure 15.

Recent tests have shown that with a slightly greater platinum content in the gel an SO_2 gas of 10 per cent concentration can be successfully used. The acid output of existing plants can therefore be readily increased by this means without any capital expenditure beyond the introduction of silica gel mass.

Very interesting and successful results have been secured in the removal of hydrogen sulfide from illuminating gas by means of silica gel impregnated with iron oxide (Fe_2O_3). Other metallic oxides or metals can be used, but the one mentioned is the smoothest in its operation.

The removal of H_2S depends upon the primary reaction

$$2H_2S + O_2 \rightleftarrows 2S + 2H_2O$$

The catalytic gel in the reaction chamber or the gas to be treated is heated so that a temperature of 200° to 210° C. is maintained during the catalyzing reaction. This reaction takes place readily and continues with 100 per cent efficiency for a considerable period, depending upon the concentration of H_2S in the gas. The sulfur formed, deposits in the base of the catalytic chamber.

Theoretically, one volume of H_2S requires 2.5 volumes of air, or the oxygen equivalent thereof, to completely oxidize H_2S to sulfur. If the illuminating gas is deficient in oxygen, a sufficient amount of air can be added to make the oxygen about 50 to 60 per cent in excess of theoretical.

Some SO_2 is also formed to a small extent in the reaction, especially if the reaction temperature goes over 210° C. This can readily be removed by the introduction of ammonia gas, which precipitates the SO_2 as $(NH_4)_2SO_3$, and which is recoverable. The ammonia for this purpose should be added after the gas has left the reaction chamber.

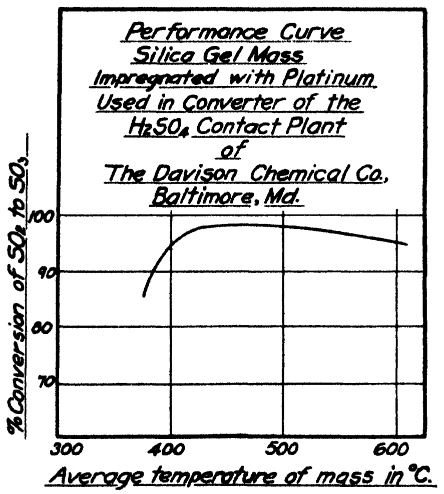

FIG. 15.

The gel, after a time, loses its high efficiency and allows a trace of H_2S to pass through unoxidized. This is due to the gradual formation of iron sulfide. When the break-point is reached the gas is switched to another gel-filled container and the "spent" gel is easily regenerated by passing air through it at 480° to 510° C. for a short time, after which it is again ready for use. The gel can be regenerated indefinitely in this way, its activity being in no way impaired.

Silica gel impregnated with Fe_2O_3 and also other metal oxides and metals, has been used successfully for eliminating some of the organically combined sulfur compounds which are found in gas, e. g. CS_2. The carbon disulfide is converted to hydrogen sulfide as follows:

$$CS_2 + 2H_2 = 2H_2S + C$$

The gas containing CS_2 is passed through a tube containing impregnated gel at a temperature of about 400° C., whereupon the above reaction takes place practically completely. The gel will operate over a considerable period of time before dropping in efficiency, after which it can be regenerated by burning out the carbon with heated air. The H_2S formed in the reaction can be removed as described above.

The commercial use of silica gel has been developed and successfully applied in many fields by The Silica Gel Corporation of Baltimore, Maryland. These applications include the purification of light oil for the production of motor benzol, refining of petroleum distillates, dehydration and purification of carbon dioxide, hydrogen, oxygen, nitrogen, helium, recovery and dehydration of chlorine, air conditioning systems, drying blast for blast furnaces and cupolas, refrigeration for transportation of perishable products and general domestic uses including dairies, cosmetic and medicinal uses, etc. etc.

Colloid Factors in Water Supply

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Colloidal phenomena are prominent in nearly every phase of water supply. They are involved in a study of sources, distribution, purification, and application in the industries.

Purification perhaps, demands more attention from the chemical engineering point of view; hence it has been the subject of more extensive colloidal studies. Colloidal phenomena have a part in removal of oxidizable impurities by aeration: in removal of suspended impurities by settling, coagulation, sedimentation and filtration, etc.; in removal of living organisms as with copper, chlorine, or ozone; in removal of dissolved impurities by softening, in lime soda, zeolite treatment, boiler compounds, etc.; and in removal of color, taste, or odor by adsorption.

Colloidal phenomena are also involved in the application of water in many of the industries, the most generally important of which perhaps is steam-making. Here the major issues: foaming, corrosion, and incrustation, all involve colloidal reactions. Waters for the textile industries: wool, silk, cotton, artificial silk. demand consideration from the colloid point of view, as do the supplies for such operations as dyeing and bleaching, papermaking, tanning, sugar refining, brewing, etc.

In brief, no important water-consuming industry today can afford to overlook a study of the colloidal characteristics of its water supply, or of the processes and reactions in which that supply is involved.

Colloids in Water Sources.

Rain Water. When water descends through the atmosphere, it carries down relatively small amounts of impurities. These are, principally, dissolved gases and suspended matter. The latter is probably derived, mainly, from colloidal organic substances, such as pollen, yeast, molds, bacteria, dust, etc. However, rain water seldom displays the phenomena associated with high concentrations of colloidal matter.

Surface Waters. When rain water strikes the earth's surface, it begins to accumulate impurities, depending in quantity and quality on the nature of the area from which it is derived.

In mountainous regions the rain water quickly finds its way among the more or less barren rocks into the streams. Such water from its short contact is not heavily charged with impurities. If suspended matter is picked up, it is usually coarse and settles out quickly, except in times of freshet. If colloidal matter were acquired, the scouring and stirring action of turbulent flow would soon bring about coagulation and removal of such matter. Mountain streams are thus usually relatively clear, pure, and free from colloidal

matter. The Columbia river in Oregon or the upper Savannah river in Georgia are typical of such rivers.*

Surface waters from prairie or plain, on the other hand, are derived by slow flow over, or percolation through the soil and are, therefore, heavily charged with matter dissolved or carried in suspension. Coarse suspended matter, like sand, is transported or deposited according to the seasonal variations in rate of flow. Fine suspensoids, like clay, however, are retained much longer and may contribute more or less matter of an inorganic colloidal nature, such as silicates, to the water. The Missouri, for instance, is a typical illustration of a river which is almost invariably muddy.[1] In this water the suspended matter is so finely divided that samples must stand for many days to clarify by settling, while attempts to filter through any ordinary means result either in a cloudy filtrate or a choked filter.

Swampy regions where the water flows very slowly will be heavily charged with organic matter of a peaty or humic acid nature. Such matter has a marked tendency to contribute organic colloidal substances to the water. These substances are often apparent by reason of the color, taste, or odor which they impart. By their presence also they may have a peptizing effect on inorganic suspensoids, causing them to pass into the colloidal state in larger concentration. An illustration of swampy-colored water is found in the familiar Florida Everglades; or in Tampa where the untreated water is so heavily charged with coloring matter as to appear at times as dark as tea. The nature of coloring matter will be discussed more in detail in connection with methods of purification.

Ground Waters. Waters which have found their way deep into the ground and are derived from wells or springs carry, in general, more dissolved, but less suspended, impurities. Such waters will usually be largely filtered by percolation, through various substrata, and as they come to the surface will generally be free of suspended matter. But on exposure the change of conditions may develop in some ground waters colloidal matter of a pronounced type. Thus oxidation may convert dissolved manganese or iron to insoluble, but colloidally, suspended matter. Reduced pressure may liberate carbon dioxide, causing the precipitation in colloidal form of carbonates. Such matter becomes apparent as a haze in the depth of a spring, for example, but usually disappears shortly. This effect is apparent in the big springs in the Ozark region; e.g., the spring at the head-waters of the Meramec river.[2]

The influence of exposure may favor the growth of organisms which convert mineral matter, particularly iron and manganese, into suspensions of an organo-metallic nature which may become very troublesome; e.g., deep wells near Tegel lake, a part of the Berlin water supply, had to be aerated and filtered; and the infiltration gallery at Newton, Mass., had to be partially rebuilt as a result of the iron contamination.[3]

* Certain glacial waters seem to constitute an exceptional group. Their low temperature enables them apparently to absorb unusual amounts of atmospheric carbon dioxide, which, in turn, increases the solvent or dispersive action of the water on many minerals, especially limestones. Subsequent settling of coarser material, and precipitation of colloidal particles due to chemical reactions or to escape of CO_2 as the water warms up, may give the water in glacial streams or lakes marked blue or green colors. Phenomena of this kind are observable in Switzerland and especially in the Canadian Rockies. The blue color of the Mediterranean and of coral lagoons is perhaps in part due to an analogous precipitation of colloidal particles of carbonates, sulfates, etc. The color developed seems dependent on particle size, which in turn depends upon local conditions. Thus Lake Louise is a greenish-blue, Lake O'Hara and Emerald Lake are greener, while the Mediterranean at Amalfi, for example, is nearly cerulean blue. Sea salts cause speedy precipitations; whereas in glacial lakes and streams the velocity of flow, the nature of salts and colloidal protectors in waters added by tributaries, the size and shape of basins—all of which incidently determine speed in drop of temperature—are factors affecting the size and persistence of the particles whose diffraction of light give "color." See J. Alexander, *Science*, 61, 312 (1925).

Pollution. All natural waters in thickly populated regions are subject to contamination by sanitary and industrial wastes which add quantities of further impurities to those already naturally present. Many of these impurities are of a colloidal nature, such as tannery wastes, textile wastes, sewage, and the like; and while not of natural origin, they have come to be recognized as an important contamination in most surface water supplies, as are also the incidental micro-organisms.

From the colloid point of view then, a water supply may carry any or all of the various types of colloidal impurities. There may be present inorganic matter, such as silica and silicates, iron or other metallic oxides; organic matter, such as peat, humic acids, plant or animal residues; bacterial matter or minerals associated with bacteria; and finally, the many varieties of waste matter from sanitary a .d industrial pollution.

Colloid Factors in Distribution of Water.

The collection, storage, and distribution of water may be influenced by colloidal phenomena, either through matter present in the original water, through matte contributed to it, or through the effect of such matter on the water system.

Impounding Lakes. In the building of dams or retaining walls, water is often caused to flood areas which have previously supported a dense growth of vegetation, or which may have been covered with a heavy deposit of loam or humus. Areas of this nature are liable to contribute soil colloids which may impart color, odor, or taste to the water.

Such flooded vegetation has been recognized as the cause of the trouble, and attempts have been made to eliminate it by removal of surface dirt over an entire area to be flooded. Such stripping which is obviously costly has met with only partial success, probably not commensurate with the cost involved. The Upper Croton reservoir of the early New York City supply was stripped, but in view of later experience the lower reservoir was not stripped. In present-day practice soaking and spilling about three times is generally found to be satisfactory and less expensive than stripping.

Micro-organisms often give trouble in reservoirs which at certain seasons may become literally hotbeds for the growth of various types of microscopic forms, which will contribute colloidal impurities to the water. The combined influences of warmth, sunlight, and quiet are all contributing factors which may sometimes be very difficult to alter. In certain regions reservoirs must be covered wherever possible to exclude sunlight, and thus inhibit microscopic growths. In Bermuda, for instance, where the climate is temperate, but the sun is hot, raw water cannot be stored in the sunlight for even forty-eight hours without becoming green from the prolific growth of chlorophyceae. All storage tanks in the region are, therefore, constructed with covers to keep out the light.[4]

Where covering is impractical, copper sulfate treatment is often resorted to in order to prevent the growth of the organisms and the resultant colloidal contamination. This treatment was first proposed by the U. S. Department of Agriculture. The first application was in the Park lakes in Brooklyn, then at Mount Prospect, and Croton Lake where it met with such success that the use has become general.

Water Mains. In distribution systems or reservoirs several types of trouble may be traced to colloidal phenomena. For ferruginous or man-

ganiferous waters, growths which thrive in such waters may become very troublesome at certain seasons, and frequent screening is required. Softened waters may leave after-deposits, or waters of low pH may give red water trouble.

Iron and manganese are converted by crenothrix organisms from solution or colloidal suspension to gelatinous stringy masses which may be exceedingly detrimental, especially to filtering equipment and conduits. Thus the sand filters at Rotterdam which derived their water from the Maas river were so badly fouled some fifty years ago that they were abandoned. Today such organisms can usually be eliminated by methods similar to those used for other micro-organisms.

Incrustations sometimes occur in distribution mains where there is a mechanical scouring action or turbulence causing the deposition or precipitation of colloidal matter from the water. This is particularly noticed in the conveying of water which has received a lime-soda softening treatment from which it may retain magnesium or calcium salts in colloidal or supersaturated solution. The alleviation of this difficulty is procured by modifications of the water treatment as described later in that connection.

Red water occasionally gives trouble in certain water pipes, particularly, the systems within private properties, and especially the hot water systems. This rusty discoloration is due to colloidal ferric iron in the water and is usually traceable to the effect of dissolved air or oxygen on the walls of the iron pipe. The effect is noticed more frequently with soft water and obviously more so with hot water. In New York City the water is so soft that incrustation in water heaters takes place very slowly, or not at all. Here it is, therefore, not uncommon to find the water in hot water pipe lines running brick red from the iron contamination originating within the heater system.

This trouble may be largely reduced by use of non-corrosive plumbing, but it is often feasible to relieve the situation by suitable water treatment. If the water contains much carbonic acid, it may be rendered less corrosive by addition of small amounts of quick-lime or soda for correction of the pH, as pointed out by W. A. Taylor and others.[5, 6] If it carries an excess of CO_2 from recarbonation after softening, this may be reduced by proper control.

The water-handling problems of a colloid nature are associated in general with corresponding problems of treatment or purification, and these are considered in more detail under the appropriate headings.

Colloid Factors in Water Purification.

Modern water purification may involve any or all of the present-day operations of aeration, sedimentation, coagulation and settling, filtration, decolorizing and deodorizing, softening, etc., and colloidal phenomena may be involved in all of these treatments.

Aeration. For removal of dissolved gases and odors, aeration is often resorted to and in this application colloidal phenomena are seldom prominent. But it is applied also for oxidation, particularly of iron, and here the iron (or manganese) may appear in colloidal form. Under such conditions considerable trouble may be experienced and a further treatment by filtration, or percolation, may become necessary.

Details of such treatment are discussed by H. Thiel[7] and C. H. Hurd[8] covering various conditions and involving addition of oxidizing agents, such as manganese dioxide to the filtering medium, or the use of coke, or even activated charcoal for alleviation of serious cases.

Reactions. The formation of colloidal ferric oxide * is familiar and is due to a combination of circumstances. Prior to aeration the iron may be present in ferrous form and the alkalinity of the water may not be sufficient to cause complete hydrolysis of the ferrous salts; thus,

$$FeCl_2 + 2HOH = Fe(OH)_2.2HCl$$

to ferrous hydroxide which is soluble about 6 p.p.m. But on oxidation, thus,

$$2Fe(OH)_2 + O + H_2O = 2Fe(OH)_3$$

the first reaction will be carried toward completion with resultant precipitation of the iron, since ferric hydroxide is soluble not over 0.3 parts per million. Furthermore, the ferric oxide has a tendency to become highly hydrated as discussed in detail by Weiser,[9] and this factor together with its insolubility accounts for its appearance in the familiar colloidal or flocculated form.

Sedimentation. Frequently the first opportunity for removal of suspended matter comes through natural sedimentation, for impounding reservoirs are often at the same time sedimentation basins. Coarse matter and some finer matter may be here eliminated, but truly colloidal material cannot thus be entirely removed. It is sometimes feasible, however, to introduce a coagulant in such a reservoir, and thus to aid the removal of the finer matter by adsorption in the resultant floc.

An example is cited by W. Brush.[10] During November, 1926, very heavy rains resulted in turbidities around 100 in the Schoharie and Ashokan reservoirs of the Catskill system of the New York water supply. Examination showed that prolonged standing would not satisfactorily remove this turbidity, but that clarification with soda ash and alum would accomplish the desired result. The soda ash was introduced into the aqueduct at the Ashokan reservoir 75 miles above the Kensico reservoir and the alum was added to the aqueduct at Pleasantville three miles upstream from the Kensico reservoir. The floc settled in the Kensico reservoir and a satisfactory water was produced. The treatment was continued from December, 1926, until May, 1927.

Coagulation and Settling. Colloidal matter and finely divided suspensoids are commonly removed by coagulation and settling in specially designed equipment used for purification purposes. Thus, if a water contains iron or alumina in solution, as, for example, an acid factory waste or the water from a highly mineralized region, simple addition of lime or soda may be used to alter the pH so as to promote hydrolysis of the metallic content to hydroxide or oxide hydrosol. This may rapidly flocculate and settle out, thus

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightleftharpoons 3Fe(OH)_3 + 3CaSO_4$$

As an example of such a case the municipal supply of Worcester, Mass., may be cited. Here the water carried plenty of iron from the Washburn Wireworks, so that only lime need be added in the course of purification.

If an alkaline water contains little iron or alumina but carries an excess of carbonate, for example, then addition of alum or iron sulfate may be resorted to. The alkalinity of the water will promote hydrolysis of the added

* See paper by I. N. Friend in this volume. J. A.

salt with subsequent flocculation and precipitation as above. Cases are not common where lime is never used, but many plants find the use of alkali necessary only occasionally, as, for example, the purification works at Little Falls, N. J., where the water from the Passaic River is usually alkaline enough to permit the omission of lime or soda.

But in the average case addition of both iron or alum and lime or soda ash is found desirable in order to introduce the flocculable matter, and then to alter the pH for coagulation. This treatment has been standardized in its application to many municipal and industrial supplies. This system with or without additional refinements is in use in Cincinnati, Baltimore, Philadelphia, and many places throughout the Middle West.

Reactions. In the purification of water by coagulation and settling, certain fundamental factors are involved, such as nature of coagulum, size of aggregates, apparent density, completeness of reactions, etc. These factors are controlled by quantity of addition agents, thoroughness of mixing, time of agitation, pH control, electrolyte concentration, and more recently by quality or type of secondary addition agents, modification of treatment cycle, etc.

The equations for the reactions taking place when alum is added to water indicate that it goes into solution with formation of aluminum ion (Al^{+++}) and sulfate ion (SO_4^{--}), thus:

$$Al_2(SO_4)_3 \rightleftharpoons 2Al^{+++} + 3(SO_4)^{=}$$

There are present also in the solution hydrogen and hydroxide ions from the slight ionization of the water, thus:

$$HOH \rightleftharpoons H^+ + OH^-$$

Since aluminum hydroxide is a weak base, there will be a tendency for formation of un-ionized hydrate, thus:

$$Al^{+++} + 3(OH)^- \rightleftharpoons Al(OH)_3$$

and since the solubility of this hydrate is extremely low, it will tend to come out of the solution in the form of a colloidal precipitate:

$$\underset{\textit{dissolved}}{Al(OH)_3} \rightleftharpoons \underset{\textit{solid}}{Al(OH)_3}$$

The law of mass action thus far governs the reactions, so that as hydroxide ion is removed, the concentration of hydrogen ion builds up to the point where aluminum hydroxide will no longer be precipitated. These reactions are discussed by M. Pirnie [11] in a detailed study of water purification from the angle of colloid chemistry. The alteration of the hydrogen-ion concentration, therefore, has an important effect on the precipitation.

Hydrogen-ion concentration is frequently adjusted by the expedient of adding quick lime or sulfuric acid. According to W. A. Taylor,[12] the optimum pH for the majority of waters lies between 5.5 and 7.0 varying with the character of the water to be treated.

But the pH of pure $Al(OH)_3$ is about 8.8, hence at pH 5.5 to 7.0 as mentioned above, the precipitate will not be pure hydroxide, and here the colloidal nature of the precipitate comes into profound significance. It is found at such hydrogen-ion concentrations that the composition of the precipitate is altered by adsorption of other ions so that if sulfate is present, e.g., there will be present along with the alumina a varying amount of sulfate radical E. S. Hopkins[13] has shown that as the pH decreases sulfate increases so that "when 3 mols NaOH are present per mol of aluminum, the floc approximates the composition $5Al_2O_3.3SO_3$," for example. As mentioned below, the nature of the adsorbed ion affects the quality of the floc.

As pointed out also by Delaporte and Manuel[14] $Al(OH)_3$ acts as a positive sol and is coagulated by negative ions; e.g., sulfate released from the alum. The floc, being a colloidal gel and having an enormous surface, exhibits great adsorbing powers which are responsible for its removing suspended matter, color, and organic substances.

The importance of other anions is emphasized by L. B. Miller,[15, 16] who regards the chemical factors in the following order of importance: (1) a certain minimum amount of Al^{+++} ion; (2) an anion of strong coagulating power; (3) properly adjusted hydrogen-ion concentration. He states further that of all the anions studied, sulfate yields a floc best suited to water clarification, it being rapid settling and compact.

That sulfate ion should be more effective than chloride ion, for example, is in agreement with the general principle of the superiority of divalent over monovalent ions. The pH range over which aluminum sulfate is thus effective (5.3 to 8.7 with a maximum at 5.5) is much broader than that for aluminum chloride (7.8 to 8.6).

This is in general agreement with the experiences of N. L. Banerji[17] in the clarification of the Calcutta water supply. He considers that the mechanism of the reaction can be divided into two parts: (a) action of unhydrolyzed alum, and (b) action of hydrolyzed alum. The aluminum ion from unhydrolyzed salt is the most potent factor, with hydrogen ion coming second, and aluminum hydroxide, formed by hydration, of third importance. In this case addition of sulfuric acid to a too alkaline water until the pH is reduced to about 7.0 results in a saving of alum.

A similar observation has been made by J. R. Baylis[18] in the Baltimore water supply, who states that by actual test, the use of 5 tons 66° Bé. acid with 7.2 tons alum enabled a daily saving of about 80 dollars for chemicals. The excess acidity thus produced was then neutralized by addition of lime.

The additional coagulating ion, such as sulfate, need not be derived from acid, but may originate from any sulfate salt as shown by Peterson and Bartow.[19] These investigators show further that salts of weak acids form buffers which "practically invalidate" the results of pH control, or perhaps the effect is better described as automatically controlling pH irrespective of external changes within reasonable limits. They mention, particularly, oxalates, tartrates, and phosphates, though the effects are by no means limited to these salts.

Specific Addition Agents. For use with or without alum several valuable agents have come into prominence within the past few years and, perhaps, chief among these is sodium aluminate. "Aluminum hydroxide solution" was described in 1923 as a new coagulating agent by J. W. Coxe, Jr.[20] Directions were given for the preparation of a solution containing so-called sodium aluminate which gave an immediate precipitation on addition to excess water.

The superiority of this agent for clarifying water was ascribed to its speed of precipitate formation.

More recently the advantages involved have been the subject of considerable study and the agent under the name of sodium aluminate is now in use in many purification plants. P. W. Evans [21] has listed four main advantages in its use as follows: (1), increased plant capacity, due to more rapid settling; (2), less causticity, giving less foaming in boilers; (3) avoidance of increased alkaline sulfates which would result from alum or copperas dosage; (4), elimination or material reduction of after precipitation.

Similar advantages are reported also by Ripple, Turre, and Christman,[22] who have made use of it in treatment of the Denver water supply and find that in addition to the above cited advantages, the average filter run was increased about five hours or 20 per cent while the average wash water requirement was reduced from 2.38 to 1.88 per cent. Christman [23] and Moberg [24] have summarized the advantages and disadvantages of this agent in a recent technical bulletin.

The actual reactions involved in the use of sodium aluminate according to Morse, Hechmer, and Powell,[25] who have studied its use at the Washington Suburban Sanitary District, are not clearly understood as yet. The obvious apparent difference is its more rapid and larger floc formation as compared with alum. Sodium aluminate solution represents a high concentration of soluble aluminum salt with a strongly alkaline reaction, instead of the acid reaction of alum. Simple dilution with neutral water, therefore, permits immediate hydrolysis to alumina, as distinguished from the necessity of neutralization of aluminum sulfate before it becomes hydrolyzed. Furthermore, the precipitated floc may be pure alumina while in the case of alum the floc, as pointed out above, will not be pure alumina unless a pH of 9 or more is maintained; at all lower alkalinity values the alum precipitate adsorbs increasing amounts of sulfate. In the alumina treatment this in effect amounts to securing the full value of aluminum ion; but in the alum treatment only a partial value is had unless the alkalinity is excessive.

Sodium aluminate may react furthermore within the limits of the quantities added (from ⅛ to 1 grain per gallon) as a powerful buffer salt, for it is the salt of a strong base and a weak acid, H_3AlO_3. The acid strength is, moreover, still lower because of its extremely slight solubility. Hence, in accordance with the principles of buffer salt action the effects of variations in pH are minimized when sodium aluminate is used, reducing the necessity for use of other pH controlling addition agents. The pH, whatever it may be, as pointed out by Moberg,[26] is but little affected by the sodium aluminate.

A further action of sodium aluminate, noted by several of the investigators above cited, is its tendency to offset the inhibitory action of some colloids on proper coagulation. This might perhaps be better stated by saying that certain colloids resist the formation of, and adsorption in, the floc produced by alum, but they are readily adsorbed by the aluminate floc. For example, when finely divided clay is present in a water, large doses of alum sometimes fail to produce the desired clarification; whereas sodium aluminate, in a concentration of perhaps 0.2 grains per gallon, is effective.

The reasons for this difference have not been established but may perhaps be found in the difference in the effective electrical charge on the aluminate floc as compared with that on the alum floc in which a large percentage of sulfate is already adsorbed.

Another specific addition agent which has been advocated by Moberg and

Partridge [27] is called ferric alumina and is described as a solution of hydrous alumina peptized by addition of ferric chloride. These investigators accept the assumption that "the degree of reactivity of any common coagulant is dependent upon the amount and type of other salts or colloids present in the water" and such coagulant reaches its ultimate efficiency only at a definite isoelectric point.

The new addition agent represents a further step in the same direction beyond sodium aluminate. Just as the latter agent is superior to alum because it more quickly forms a good floc (since it carries its own alkalinity along with it and does not depend for proper reaction on independent adjustment of the pH of the water), so peptized hydrous alumina altogether obviates the necessity of reaction because it is already a prepared colloidal material. If, therefore, it can be protected from the inhibitory peptizing effects of oppositely charged colloids which may be present in the water, then it should be a superior addition agent.

The new agent then consists of a hydrous alumina gel prepared by reaction of e.g., aluminum chloride with sodium aluminate; the soluble salts are washed out of this gel and ferric chloride is added in a proportion of from one to three parts per part of alumina depending upon the purpose for which it is intended.

The ferric chloride tends to keep the alumina peptized or "fresh" until added to the water. "The chloride then hydrolyzes liberating the alumina and itself forming a colloidal precipitate with protecting action and additional absorbing power."

The resultant product has given uniformly good results with use of from 1 to 1.5 grains per gallon when alum requirements fluctuated between such wide limits as 1.5 and 4.5, or sodium aluminate between 0.3 and 1.0 grain per gallon.

Mechanical Treatment. An important factor in the control of coagulation aside from the use of addition agents is the mechanical treatment to which the water is subjected. Thus, duration and activity of mixing, rate of addition, and number of stages in the course of application, etc., are all worthy of attention. The chemical reactions are rapid, but the colloidal adsorptions and particularly the flocculations take time; the desirability of rapid addition of reagents has been pointed out by Ellms [28] and others, and the necessity of thorough mixing is well known.

The use of agitation has proved advantageous, for example, in an instance cited by Capen,[29] who found that in the Bridgeton plant when the floc did not form, blowing with air gave the desired mixing and resulted in proper flocculation. In Baltimore Hopkins [30] studied the condition of the water at several "turns" during its course of a half hour through the baffle channel. It was shown that good mixing was obtained after the first few turns, but that less time was required for sedimentation after each subsequent turn and samples at the extreme end of the basin always settled in the shortest time, proving the beneficial effects of agitation.

The value of multiple stage coagulation has been demonstrated by Bahlman and Evans [31] at Cincinnati where extensive tests showed a double treatment added to the normal cost, 86 cents per million gallons. This treatment was most effective in the warm weather period during which time the increase in length of filter runs was 30 to 65 per cent and the reduction in washwater was 25 to 40 per cent. The double coagulation materially improved the quality of the filtered water and reduced the chlorination requirements. Similar experiences are cited also by Armstrong.[32]

Filtration. Water treatment frequently includes filtration through sand and this operation may or may not be preceded by sedimentation or coagulation. Two principal methods are recognized, called, respectively, slow and rapid sand filtration, and each of these involves colloidal phenomena.

Slow sand filtration is usually applied without prior treatment to water containing more or less visible suspended matter. Such water is flowed through the sand bed at a slow rate of perhaps one to two million gallons per acre per day. Under these conditions, suspended matter in the water soon forms a skin or layer in the upper surface of the sand. This matter acts as an adsorbing and filtering film but eventually chokes up the surface until after a few months the rate of flow is too slow. The bed must then be drained, dried, and cleaned. In this operation it is important to leave enough of the old accumulation to serve as a nucleus for starting the new adsorption cycle.

Rapid sand filtration is applied in the case of waters to which a coagulating agent has been added for the purpose of quickly forming a gelatinous layer. In such cases the sequences of operation will usually consist of adding lime or alum or both, mixing by power agitators or baffles, allowing the water to remain in a basin or reservoir for one-half hour or more to get good coagulation, and then filtering. Such a treated water is flowed through the sand at a rate of 100 to 200 million gallons per acre per day. Under these conditions the filter becomes clogged after six or eight hours of operation. It is then regenerated by reversing the direction of flow and forcing clear water up through the sand for a few minutes until the surface accumulation has been flushed to the sewer when the cycle of operations may be repeated.

Reactions. The phenomena in slow filtration are essentially all colloidal. The operation was probably first employed in London in 1829 by James Simpson of the Chelsea Water Works Company before the science of colloid chemistry, or even bacteriology, was known; but the removal of bacteria by adsorption was none the less effective, and the reduction in typhoid death rate was an astonishing accompaniment of the uncertain effort to remove mud and visible pollution from the water. The original sand beds were constructed some ten feet thick, since mechanical filtration was the only expected effect. But in fact the layer of matter removed from the water and accumulating in the upper surface of the sand soon forms a continuous skin, gelatinous in nature, and highly adsorbent. It acts, therefore, first as an impervious filtering medium, completely clarifying the water and rendering the lower portions of the sand bed unnecessary. It acts also as a powerful adsorbing medium, removing from the water colloidal substances, such as bacteria, coloring matter, tastes, odors, etc., which would pass through an ordinary filter.

In rapid sand filtration the phenomena include a combination of the reactions discussed under coagulation with those described above. Modern filtration practice, therefore, involves the routine measure and control of pH in raw and treated water, composition, and proportions of addition agents, turbidity and bacterial counts on influent and effluent, as well as frequent tests of variation in coagulating and adsorbing power of the artificial floc produced.

Softening. Modern water purification practice often involves softening, especially for industrial purposes or for municipal supplies which are unusually hard. Softening may be accomplished by the use of lime soda, zeolite, boiler compounds, soaps, and powders, etc. The use of soap introduces a whole series of colloidal phenomena which are more appropriately discussed under other headings and are beyond the scope of a chapter on water. The lime soda and the zeolite processes, however, involving more specific colloidal reaction, may receive consideration.

The lime soda process. Until recently, at least, the more commonly employed was the lime soda process which consists essentially of the addition of hydrated lime to precipitate bicarbonate hardness and the addition of sodium carbonate to precipitate sulfate hardness. This process is usually carried out in a sequence of operations, consisting first in metering the raw water through a device which automatically proportions the dose of chemicals to be added; second, in mixing the water and chemicals in a baffled channel, or in power-operated mixing chambers; third, in allowing the resultant precipitate to drop out in a settling basin or tank; fourth, in filtering the resultant effluent usually through sand; and fifth, frequently, in after-treatment of the filtered water with carbon dioxide, chlorine or other special agents.

The chemical reactions involved are as follows:

$$Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O$$
$$2Ca(OH)_2 + Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$$
$$Na_2CO_3 + CaSO_4 \longrightarrow CaCO_3 + Na_2SO_4$$
$$Ca(OH)_2 + Na_2CO_3 + MgSO_4 \longrightarrow CaCO_3 + Mg(OH)_2 + Na_2SO_4$$

Of course these reactions do not proceed independently nor do any of them go to completion. Rather the whole system becomes an ionic complex, in which the equilibria are approached simultaneously. Thus far the reactions are all ionic and equilibrium is, therefore, probably reached at once. But the actual removal of the constituents includes their precipitation in insoluble and filtrable form and involves additional equilibria as expressed by the second part of the following equations:

$$Ca^{++} + CO_3^{=} \rightleftarrows \underset{\textit{dissolved}}{CaCO_3} \rightleftarrows \underset{\textit{undissolved}}{CaCO_3}$$
$$Mg^{++} + 2(OH) \rightleftarrows \underset{\textit{dissolved}}{Mg(OH_2} \rightleftarrows \underset{\textit{undissolved}}{Mg(OH)_2}$$

There is a considerable tendency for the second part of these reactions to proceed slowly; i.e., the solutions tend to remain supersaturated as noted by Schoch,[33] for example, with the result that the quantities of calcium carbonate and magnesium hydroxide which remain in solution during the normal course of the softening operation are greater than would be expressed by the solubility products for these two constituents. Thus, the true solubility products would predict that under suitable conditions calcium carbonate would be soluble about 33 mg./liter and magnesium hydroxide about 3 mg /liter. To reach this condition for $Mg(OH)_2$, the pH must be raised to about 10.8 according to Baylis.[34] But while theoretically the residual hardness should be 35 to 36 p.p.m., yet actually after the usual treatment cycle, it will frequently measure 55 or more parts per million. Careful examination of a treated water with this high residual hardness reveals the fact that the excess matter may not be in true supersaturated solution, but exists perhaps in colloidal suspension.

Moreover the results of the condition soon become apparent in the softening and distribution system, for after operation of the filters for some time, it is frequently noted that the average size of the sand grains is increasing. This may be due simply to mechanical washing out of the smaller grains, or it may be due to a gradual accumulation of an incrustation on the sand. This

incrustation will be found to consist of the suspected calcium and magnesium salts and is not usually confined to the sand filters alone, but may occur throughout the distribution pipe lines, especially at curves and irregularities where a scouring action or turbulent flow may occur.

To overcome the difficulty two methods of procedure are possible: either conversion of the residual hardness to a truly soluble form, or complete precipitation and flocculation of the substances down to their true solubility limits. The first of these methods leaves a higher residual hardness in the water, but may be readily carried out with certainty; the second produces a softer effluent, hence it is preferable whenever it can be effectively accomplished.

To carry out the first process of redissolving, it is necessary only to convert the residual insoluble carbonate or hydroxide to the more soluble bicarbonate by addition of carbon dioxide, after settling and before filtering, thus:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$
$$Mg(OH)_2 + 2H_2CO_3 \longrightarrow Mg(HCO_3)_2 + 2HOH$$

These are simply the chemical equations expressive of the net results; but actually (*vide supra*) the whole change consists in a shift of equilibria in which the concentrations of carbonate and hydroxide ions are reduced by introduction of carbonic acid with which they combine to form the very slightly dissociated bicarbonate ion.

Obviously it is easy to shift the equilibria as far as is desired by introduction of sufficient CO_2. In fact a previously formed incrustation may be again gradually dissolved by such a procedure. But herein lies another objection to the practice, since lack of extreme care in the addition of the CO_2 may result in production of a water of such low pH as to be distinctly corrosive to pipe lines or industrial equipment.

To carry out the second process, that of elimination of the supersaturated or colloidally suspended matter addition agents of a different type are used. Thus, an increase in pH or hydroxide alkalinity will so react on the solubility product equilibrium as to reduce the concentration of Mg and Ca. That is, as emphasized by Baylis,[35] in more alkaline water these salts are less soluble, reducing the tendency to supersaturation. Furthermore, the introduction of a rapid-forming highly adsorbent floc will tend to remove the colloidally suspended excess of these salts. Both of these conditions can be brought about simultaneously by addition of sodium aluminate; and this reagent, already described as valuable in clarification practice, is now highly regarded in softening practice.

To illustrate, Paul M. LaBach [36] has reported the use of sodium aluminate in 25 plants of the Rock Island Railway Lines with several advantages: (1), increased plant capacity; (2), less residual hardness in treated water with smaller lime soda overtreatment; (3) less alkali salts in treated water with reduction in foaming; (4), less after-precipitation and improved pipe line conditions. Another advantage cited in a committee report of the American Railway Engineers Association is the hastening of the reaction time. This committee further gives quantitative data on usage of from 1 to 3 grains per gallon of $Al_2(SO_4)_3$ or $FeSO_4$ as being less effective than 1½ grains per gallon of sodium aluminate.

But sodium aluminate has another valuable function, for it is found that at pH 9 or more magnesium aluminate will precipitate, while a sufficient excess of the reagent will tend to precipitate the calcium also as aluminate, so that

the remaining permanent hardness may be reduced to as low as 25 to 30 mg. per liter through adequate use of the reagent.

In view of the present advanced knowledge of the subject, it would appear, therefore, that a careful consideration of the colloidal factors involved should enable the elimination of many of the inherent difficulties in any modern lime-soda softening plant.

The Zeolite Water Softening Process. A system now assuming prominence is the zeolite adsorption process, consisting in the bringing of water into contact with a mass of insoluble zeolite,[37] essentially sodium silico-aluminate, which reacts with the Ca^{++}, Mg^{++}, Fe^{++}, etc., in the water, producing insoluble zeolite "salts" of these metallic radicles and leaving an equivalent amount of Na^{+} in the water. When the zeolite is spent through its conversion to the calcium and other salts, it may be regenerated by contact with a solution of sodium chloride. This converts it again to sodium zeolite leaving the calcium, etc., in the solution as chlorides which are flushed to the sewer. The zeolite is then ready for the next cycle.

The process may be traced back historically [38, 39] to Way's original papers in 1850. At present it is carried out in tanks containing the zeolite mass and provided with a system of valves for throwing the tanks into communication with the raw water source and soft water storage, or into communication with a brine chamber and the sewer to permit the passage of brine through the zeolite for the purposes of regeneration.[40, 41]

The chemical reactions may be expressed as follows:

To soften $\longrightarrow$

$$Na_2Ze + (Ca,Mg,Fe)(HCO_3,SO_4,Cl_2) \rightleftharpoons (Ca,Mg,Fe)Ze + Na_2(HCO_3,SO_4,Cl_2)$$

To regenerate $\longrightarrow$

$$(Ca,Mg,Fe)Ze + 2NaCl \rightleftharpoons Na_2Ze + Ca,Mg,Fe)Cl_2$$

In these equations Ze stands for the zeolite complex, and it is understood that the soluble reacting matter is present largely in the ionic form.

The mechanism of the reactions is a subject of considerable controversy. It is obvious that the reaction is reversible and may be driven in either direction according to the law of mass action. But it is also clear that if the reactions were merely the formation of simple chemical compounds, then the zeolite "radicle" would become appreciably soluble at some stage of the reaction. Furthermore the reaction would not reach but would only approach completion in either direction, and the zeolite "radicle" would have a definite constant composition. None of these conditions is fully realized, for the zeolite does not dissolve appreciably, the water is easily brought to "zero hardness" and the zeolite complex is of variable constitution.

The ionic explanation of the mechanism received support from Hisschemoller,[42] who referred in a rather comprehensive review to the earlier work of such investigators as Rauman and Spengel,[43] Rothmund and Kornfeld,[44] van Bemmelen [45] and others. He showed that the replacements obeyed the laws of ionic reaction, at least in so far as their dependence on concentration was concerned. At about the same time (1922) Gunther-Schulze [46] also demonstrated that in a certain measure the demands of the law of mass action are fulfilled. Later Frankfurter and Jensen [47] showed that a large excess of the replacing metallic ion results in complete exchange. They demonstrated, moreover, that the exchange reactions are more nearly complete with dilute than with concentrated solutions, an observation which gives support to the theory that these reactions are ionic.

More recently Wiegner and Jenny [48] have proposed that the base exchange depends on an ionic interchange, which in turn depends on hydration of the ions in solution. They show a direct relationship between exchange of ions and atomic volume of the ions, and propose a formula [49] for the equilibrium exchange which takes into account the dilution. Wiegener's concept is discussed by Kappen (and others), [50, 51] who advances the work on hydrolytic dissociation and maintains that the amount of replaceable hydrogen ion in permutites is small in comparison with other cations, and that the exchange reaction of other cations with hydrogen ion does not take place until a relatively high concentration of the latter is present in the zeolites. He shows further that the cations, especially aluminum, which give hydrolytically dissociated salts, are more responsible for the so-called exchange acidity. A review of these discussions is given by Jenny,[52] together with copious data and many curves.

The structure of the zeolites has been the subject of investigation through the medium of Laue and other X-ray photographic methods. Pauling [53] has demonstrated a structural unit, $8Na_2Al_2Si_3O_{11}.2H_2O$, face centered and with a structure such that water can escape, on heating, through channels along the axis (001). In base exchange operation sodium ion can escape along the same channels. Again Weigel [54] has stated that in the formation of zeolites where the silica atoms have assumed a comparatively rigid tetrahedral lattice orientation, the solvent in which the crystals form remains within the lattice without contributing to the structure. He maintains that the structure retains its rigidity under various conditions and the energy of the internal pressure is free and serves to bind foreign substances.

That the silicate served only as a suitable physical medium without playing any direct part in the exchange of bases, had been previously suggested by Vogtherr.[55]

The industrial experiences with zeolite have contributed in a measure to their understanding. The manufacture of artificial zeolites [56, 57] demonstrates unquestionably their highly complex colloidal gelatinous nature, for they are prepared by complete gelation of solutions made from sodium silicate and sodium aluminate. The zeolites must, therefore, be highly adsorbent. Regeneration is more efficient with 5 per cent than with 8.6 per cent salt solution as reported by Campbell and Davis [58, 59] in a survey of two installations for Ohio river water near Pittsburgh, while a 6 per cent brine is used according to Pierce,[60] at Springdale, Pa. The superior efficiency of these more dilute solutions is in conformity with the evidence above cited of ionic reaction.

In the light of present evidence then, it would appear that the zeolite process involves ionic reactions and that these reactions are profoundly influenced by the degree of hydrolysis or hydration of the salts and ions concerned. The actual forces involved in promoting the reactions, however, include adsorption and other surface and structural phenomena, familiar in the field of colloid chemistry.*

Organic Purification. Elimination of organic contamination from water is frequently necessary, for waters may contain living organisms of all magnitudes as well as the decomposition products of such organisms. Such matters may impart color, taste, odor, or bacterial contamination to the water, and these are almost invariably of colloidal nature.

The purification methods already considered may often effect a sufficient

* *See* remarks in Vol. I as to differentiation between chemical and physical reactions. *Also* J. Alexander, "Colloid Chemistry," New York, D. Van Nostrand Co., 1929, 3rd ed. J. A.

reduction of these impurities. Thus filtration through sand involves contact with the gel-like *schmutzdeckel,* which may adsorb most of the bacteria, colloidal matter of larger dimensions, and even coloring matter in the finest state of colloidal subdivision. Coagulation and sedimentation will obviously remove by adsorption the same general types of matter at least as effectively. Softening, if applied, will also be of value, especially if followed by efficient filtration.

But there are many cases where these methods are not used or where they are inadequate, and for such cases special methods of control have been developed. These include aeration, creation of artificial turbidity, superchlorination, use of active carbon for removal of excess chlorine, color, or odor; or combination of any of these with coagulation and filtration.

Aeration has already been discussed as a means for removal of dissolved gases and odors and for oxidation of iron and manganese. The reactions there described serve also to eliminate the troubles resulting from such organisms as crenothrix which thrive only in water carrying traces of either iron, manganese, or aluminum. Aeration also is important in the treatment of waters which have suffered recent sewage pollution, for putrefactive bacteria thrive only under anaerobic conditions. Hence, if oxygen is supplied in sufficient quantity to contaminated water, putrefaction will be prevented and oxidation of the organic matter will proceed normally.

Aeration may be accomplished by power pumping or by spray fountains if the water source has sufficient head, or by natural stream flow if a sufficient time element can be allowed. An excellent illustration of purification through aeration by stream flow is afforded in the Chicago drainage canal. When it was first put into operation a storm of protest was raised in the city of St. Louis which was taking its municipal water supply from the Mississippi river just below the mouth of the Illinois river into which the Chicago drainage canal was discharged. After prolonged litigation, however, it was definitely proven that natural aeration of the polluted drainage discharge as it flowed down the course of the Illinois river, rendered it purer than the Mississippi river into which it emptied.

Artificial turbidity may be deliberately created to control organic growths as pointed out by Lovejoy[69] in connection with the Louisville, Kentucky, water works. At this plant filter runs were seriously reduced by algae during certain seasons of the year, particularly when the natural turbidity ran low. During these periods the turbidity was increased by pumping sludge from the bottom of the preliminary settling basins to the raw water inlet of the basins. Five hours' operation of the pumps caused sufficient stirring up to give a turbidity of 500 at the inlet, instead of a turbidity of 50 or less without pumping.

This artificial turbidity performs a double function. About 80 per cent settles in the two preliminary settling basins removing a large number of organisms, thus inhibiting their multiplication. The remaining 100 p.p.m. of turbidity provides a nucleus for an excellent floc in the coagulating basin which carries down additional organisms. During this treatment the bacterial count and *B. coli* content of the water leaving the basins is lower than in the incoming raw water, demonstrating not only inhibition of algae growth, but bacterial purification as well.

Coagulation as applied in removal of inorganic impurities is often very useful for removal of such organic contamination as coloring matter.

The nature of color in water has been discussed by Thorndike Saville,[70] Joseph Race,[71] and others. The coloring matter usually encountered has been

shown to consist largely of suspensoid and emulsoid particles usually negatively charged, and to a small extent, of non-colloidal matter. This matter is derived usually from humic acid and its salts as may be demonstrated by electrolysis or catapharesis. Its colloid nature is verified also by ultramicroscopic studies carried out by Christman [72] by electrolysis or cataphoresis experiments. The isoelectric point of such coloring matter is approximately the same as the zero point of methyl red according to Race [73] and maximum removal is obtained by maximum concentration of alum that can be added without changing the disperse phase.

Reaction of the negative colloidal color with the positive nucleus of the coagulating agent (copperas or alum) gives flocculation precipitation and decolorization, but as pointed out by Whipple [74] colored waters having the negative property increased by addition of CO_2 can be better decolorized by alum coagulation. This is in conformity with the experience of Jackson, who found that the highly colored water in the Everglades region of Florida could be successfully decolorized, first, by adjustment of the hydrogen ion concentration by addition of so active an agent as sulfur dioxide, followed by the customary addition of alum coagulant.

The relationship of electrical charge to precipitation with alum has been studied also by Weston,[75, 76] who states that for proper clarification the aluminum ion must combine and precipitate the color particles. On the other hand Buzzell [77] points out that at Flint, Michigan, the use of lime has solved the color problem without the use of a high alum feed. In this plant an overdose of lime of 25 to 35 p.p.m. is given followed by addition of 10 to 15 p.p.m. of alum and ultimate neutralization of the causticity with CO_2. Apparently then, the conflicting observations of different operators on removal of color by coagulation will be reconciled only by a complete understanding of the nature, iso-electric point, and colloidal reactions of the particular coloring matter and coagulating agent in question.

Superchlorination has of late received attention as a means of removing taste and odor from water and, since taste and odor may be due to colloidal matter, it is worthy of note. If a dose of chlorine is used in excess of that for bacterial action, the excess will react with mal-odorous organic matter, oxidizing and destroying it, but causing a "chlorine taste." Dechlorination, however, may be accomplished by treatment with ammonia or active carbon, for example, and this combined treatment has been very successful with certain troublesome waters.[78, 79] A review of early work on the subject has been given by Hepburn,[80] and the more recent progress has been summarized by Howard.[81]

Activated Carbon. Within the past few years as activated charcoal has become less expensive, its use for large scale water purification has rapidly increased. The powerful adsorbing properties of charcoal and its value for clarifying decolorizing and deodorizing were known before the nature of adsorption or its colloidal significance was understood. Bone char filters have been used to decolorize and deodorize sugar solutions for many years and their use has been applied also to water where the cost was not prohibitive. Thus, for example, the distilled water prepared for beverage purposes by the Consumers Company of Chicago was rendered crystal clear and free from objectionable odors, particularly ammonia, by charcoal filters installed prior to the beginning of the present century. The application of active carbon to large scale water purification has followed the growth of knowledge of the nature of adsorption, activation, regeneration, etc., of charcoal together with the ever-increasing standards of purity demanded.

The reactions involved are essentially physical in nature and are probably in all cases largely a matter of selective adsorption of colloidal or even ionic impurities on the enormous surface of the activated carbon. That this is the case is indicated by the nature and preparation of the active charcoal and by the methods of its regeneration. It is found that, volume for volume, a more dense charcoal is more effective; that is, in a given volume a larger weight with correspondingly larger surface has correspondingly greater adsorbing power. The methods of activation consist usually of selective oxidation at relatively high temperatures by such agents as water vapor, and hence, are supposed to leave the carbon surface free of adsorbed impurities and ready to take on such. The methods of regeneration are not altogether perfected as pointed out by Carpenter [82] and may be entirely ineffective for certain types of charcoal,[83] but such results as have been obtained indicate that the regeneration is accomplished through the removal by oxidation, extraction, or distillation of matter bound by physical adsorption on the surface of the carbon.

Applications of the treatment may be made for many types of impurities. Thus, as mentioned above, it is effective for chlorine removal and for this purpose is in regular use, for example, in Stuttgart, where the treatment consists of superchlorination in two stages: filtration through sand, and then through charcoal, giving a tasteless, odorless, water. The carbon is regenerated by selective oxidation with chlorinated soda solution followed by calcium chloride solution to remove the alkali and leave a film of calcium carbonate.

Color removal also may be effected by activated carbon and the treatment is "simple, easy, and inexpensive" according to Behrman and others.[84] They recognize the color to be largely colloidal in nature, and the recommended treatment involves oxidation by superchlorination and removal of the excess chlorine together with any residual color by filtration through active charcoal, "hydrodarco." Owing to the difficulty of regeneration of the spent charcoal, it is recommended that the treatment be preceded by coagulation and filtration under carefully controlled pH conditions for preliminary removal of as much of the color as possible.

Taste and odor removal may be effected by use of activated charcoal as noted by Baylis [85] and Spalding.[86] The conditions and methods of application are similar to those for color removal except that in this case the substances to be removed are often of such small dimensions as to approach molecular dispersion in the water. Some molecularly dispersed odors are easily removed, as, for instance, chlorine, while others like chlorophenol [87] offer considerable resistance to adsorption under normal conditions.

Combination of active charcoal treatment with chemical methods of purification may prove eventually to offer the best process of water treatment where organic contamination is to be dealt with. Such a process is in operation on the waters of the Elbe river at Magdeburg.[88] In this plant the water, which is badly contaminated, is passed through double sand filtration. A treatment of 40 grams alum and 20 grams fuller's earth per cu. meter is given before the first filtration, then 1 gram of active charcoal per cu. meter before the second slower filtration. This is followed by chlorination and a good water, free from phenolic taste, results.

A recent combination chemical and active carbon installation is described by Spaulding.[89] In this plant the water is treated with excess lime, twice mixed and settled, recarbonated and filtered. During the second mixing the active carbon, "Nuchar No. 2 Fine" is added. Part of this settles out in the

second settling clarifier and is recirculated, the remainder being removed and discarded by the filters. The active carbon is expected to assist in removal of algæ odors for which a chloramine treatment is also applied.

The high quality of the product and the moderate cost of such a combination treatment would indicate that the process bids fair to supersede methods at present employed in many plants where such conditions as these must be overcome.

Colloid Factors in Utilization of Water.

The utilization of water for steam-making is its broadest application in industry, and in this connection colloidal factors are intimately involved. There are many specialized industries also where the colloid nature or treatment of the water supply are of fundamental importance.

Boiler Feed Water Treatment. Softening practice for boiler feed waters includes not only prior removal of scale-forming ingredients, but also their modification within the boiler by means of addition agents. Many of these addition agents are of colloidal nature and were in use under rule-of-thumb methods long before the nature of their action was subject to explanation.

In practice, so-called boiler compounds usually contain two classes of ingredients: first, compounds which act chemically to precipitate incrustants in combinations which give a soft non-adherent scale; and second, compounds which act mechanically to prevent close cohesion of precipitated matter in dense adherent form. The first class consisting of such substances as soda, caustic, sodium phosphate, etc., involve no important colloidal phenomena. The second class consists of all sorts of fats, starches, wood extracts, tannates, and other organic substances, as well as the newer agents, such as sodium aluminate. Even the usages of such curious compounds as old leather or an oak-board have been recorded [61] and are not without reason.

The mechanism of the reactions of organic agents is still far from completely established, but with the growing understanding of colloidal phenomena the subject is rapidly clarifying. From a somewhat non-technical point of view the subject has been reviewed by Reinhard,[62] who pays attention largely to the types of colloids which are commercially successful. He emphasizes the statement that effective colloids are those which are capable of forming a gel which will be stable under boiler conditions.

That such colloids are more valuable would be indicated by the work of Sauer and Fischler [63] through their exhaustive study of the precipitation of calcium carbonate from water under various conditions. These investigators showed that agitation and high temperature increase the degree of removal proportionately. They demonstrated further that water containing such hydrosols as gelatin, gum arabic, agar, dextrin, or tannin showed a greater residual hardness after treatment. This was explained as due to the action of these materials as protective colloids for the carbonate present, preventing its coagulation and precipitation. The same colloidal interference would of course take place within the boilers, thus markedly reducing the quantity of scale formation.

But the beneficial action probably does not stop here, for as pointed out by Stumper [64] the use of a colloid, such as humus material, not only retards precipitation but helps to keep the precipitated material in a colloidal state, thus producing flocculent spongy scale which is readily blown off. All sorts of organic colloidal substances have been proposed, from linseed oil extract [65]

to the favorite tannin, and all of those which give stable gels at boiler temperature have some value.

Inorganic colloids may also play a part in feed water treatment, for it has been recently shown that the dense silicate scale may be reduced by specific addition agents. It is probable that much of the silica in raw feed water is in colloidal or semi-colloidal silicic acid form. It is not removed by ordinary lime soda softening and when introduced into boilers is responsible for a hard dense destructive silica scale. This scale may be reduced, as shown by Christman,[66] by the use of sodium aluminate, either in the preliminary softening or as a feed water addition agent. The reagent converts silicic acid to insoluble calcium or magnesium alumino-silicate which flocculates and precipitates in spongy form. The action of this reagent has also been discussed by Holmes,[67] who contends that the sodium aluminate is molecularly dispersed in solution as a reagent.

Water in the Textile Industries. Textile fibers including wool, silk, and cotton as well as the synthetic filaments, such as rayon, are prepared for fabrication by processes which involve the use of quantities of water. All textile fibers involving as they do, enormous surfaces, have great adsorbing power. Colloidal or suspended impurities in the water will, therefore, tend to accumulate in the fibers causing a discoloration or streaked effect, and the use of water carrying such contamination is obviously out of place.

A second class of impurities, including soluble salts of iron, calcium, and magnesium, tend to unite with the soaps used in scouring, forming compounds which are insoluble or colloidal in nature. These compounds are as harmful to the goods as the first type, and furthermore, represent an economic loss in wasted soap.

The traces of certain impurities which may give trouble are sometimes astonishingly small. This is well illustrated by an experience of the large rayon plant near Buffalo. Here is was definitely established that the discoloration in the top skeins of piles of fiber through which they were running wash water was due to a trace of copper in the water which gave trouble in concentrations as low as one part in 40,000,000.*

Water in Paper Making. As in the textile industries papermaking involves a pulp with great adsorption capacity, hence colloidal or suspended impurities in the water will have an injurious effect on the product. When it is considered that from 10,000 to 400,000 gallons of water are used per ton of finished paper, the importance of pure water is evident, especially for higher grade white papers. For such products ferruginous waters are out of the question since the iron is precipitated as colloidal hydrated ferric oxide giving the pulp a brown color, and producing brown spots during the sizing operation.

The advantages of a clear pure water supply are evident in the manufacture of chemical filter paper. Here the Swedish brands are highly regarded for their superiority which is due in no small part to the clear cold mountain streams of snow water which constitute the water supply for these brands.

What is true of the textiles and paper applies equally as well in the other water-consuming industries, so that the importance of water purification methods is recognized today as never before by these manufacturers.

* Observation privately reported.

SUMMARY.

The colloid chemistry of water supply embraces many branches of the industry, including distribution, purification, and utilization of water. The problems of one branch may be intimately associated with those of another, as, for example, the removal of crenothrix which is important in storage, distribution, and filtration. The more recent and highly specialized studies in colloid chemistry have, perhaps, been focussed on those branches of water supply concerned with coagulation and adsorption, but it would be idle to say that these are the principal fields concerned. Rather, it is these branches which have presented the most obvious problems. The future will doubtless demonstrate that colloidal phenomena are associated with every phase of water supply, and that the science of colloid chemistry will give the ultimate solution to problems all the way from the original source to ultimate consumption of one of the indispensable commodities of mankind.

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It is obvious that a single chapter on the colloid chemistry of water supply can be little more than a summary of the matters presented. For detailed discussion of the several topics the reader must be referred to the original sources to which references as indicated have been freely made in citations throughout the chapter.

Crushing and Fine Grinding of Quartz

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Work of Martin and Co-workers.

1. Law Governing the Connection Between the Number of Particles and Their Diameters in Grinding Crushed (Quartz) Sand.

Martin, with Blyth and Tongue,[1] ground "Leighton Buzzard" standard quartz sand in an experimental tube mill 18" x 18", using 13.9 lbs. of sand with 247 lbs. of 1-inch steel balls. The sand had been screened, and only material passing through 20 mesh and held on 30 mesh was put in the mill. The charge was milled for varying lengths of time, from 600 revolutions to 10,000 revolutions duration, in a great number of experiments. Samples were taken from the mill and examined under the microscope, the particles being measured for mean diameter. The number of particles lying between arbitrarily chosen limits of size was listed for each sample examined. The original sand had an average diameter of 0.02748", and the ground samples were measured for mean diameters from 4.724×10^{-4} inches to 18.90×10^{-4} inches.

In another set of experiments the same graded sand was ground under the same conditions of milling for varying lengths of time. Samples were withdrawn and subjected to an air elutriation process in which the finer particles were blown up a 5-ft. brass tube, 2¾" in diameter, and settled in a dust collecting box. Experiments were carried out in many ways, as for instance by taking samples at the first period of elutriation or at the last period of elutriation, and throughout the period of elutriation lasting two hours. The air nozzle had an aperture of 0.060 inch and the air pressure was 40 cms. of water. The particles were counted and measured for mean diameter between diameters 0.333×10^{-4} inches and 5.67×10^{-4} inches in one series using $1/12$" oil immersion objective, and between 0.55×10^{-4} and 7.78×10^{-4} inches in another series using a $1/6$" objective.

In all the experiments the distribution of particles, plotting the mean diameter of particles against the number of particles, followed, not the ordinary probable error curve, but the so-called "compound interest curve." This frequency curve shows how the number of particles in any given ground sample continuously increases as the diameter decreases, and has the form

$$Y = ae^{-bx}$$

where x is the mean diameter of the particles, a and b are constants, and Y expresses the rate of increase in the number of particles corresponding to a mean diameter x. The mean diameter x represents the linear dimension of all particles between values of $x - \frac{dx}{2}$ and $x + \frac{dx}{2}$, the total allowable spread in diameter being dx. In the experiments this spread was arbitrarily fixed as

½ a scale division in the microscope, and for the ⅛" objective this amounted to 0.7874×10^{-4} inches. Thus a mean diameter x of 7.087×10^{-4} inches represented all particles (numbering N) in the range $6.693 - 7.480 \times 10^{-4}$ inches ($dx = 0.7874 \times 10^{-4}$ inches), and a mean diameter 15.75×10^{-4} inches represented all particles in the range $15.35 - 16.14 \times 10^{-4}$ inches ($dx = 0.7874 \times 10^{-4}$ inches), it being understood that the spread dx for any experiment is maintained constant.

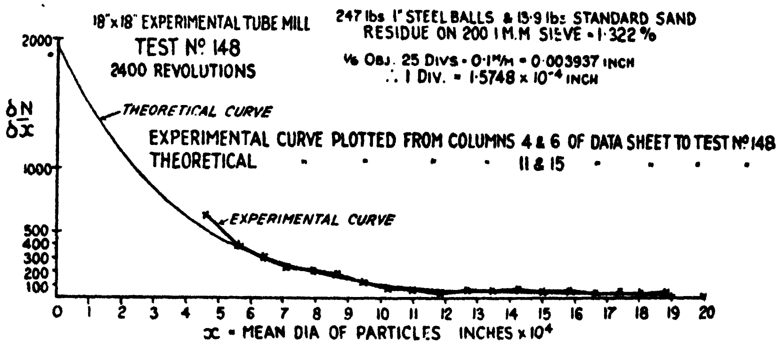

FIG. 1.

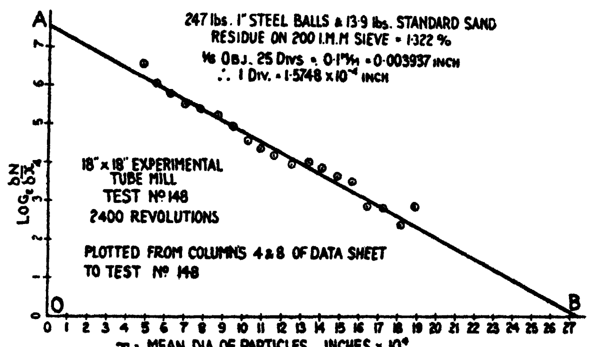

FIG. 2.

N varies with x according to the equation $N = ae^{-bx}$, and the differential $\dfrac{dN}{dx} = -bae^{-bx} = -bN$. As the diameter of particle decreases the rate of increase of the number of particles $\dfrac{dN}{dx}$ is proportional to the number of particles present of that size, at the instant the rate of increase was measured. Thus the number N increases at a rate proportional to itself, and this is the significance of the Compound Interest Law.

The data are plotted with the mean diameter x as abscissa and the number of particles N as ordinate. Instead of N the ordinate may be $Y = \dfrac{dN}{dx}$, where dN is also the number of particles in the range of diameters under consideration (having the spread dx). In both cases the curve will be the exponential curve type (*see* Fig. 1), and not the probability curve type, the latter being

expressed by the equation $Y = ae^{-x^2}$. If log Y is plotted against the mean diameter, that is, $\log \frac{dN}{dx}$ against x, a straight line is obtained which cuts the axes at significant values (*see* Fig. 2) which represents the same data as Fig. 1. When $x = 0$, $Y = a$ and indicates the number of particles present of infinitely small (zero) mean diameter. b is a ratio and may be expressed as the tangent of the angle θ which the straight line makes with the abscissa. e^b

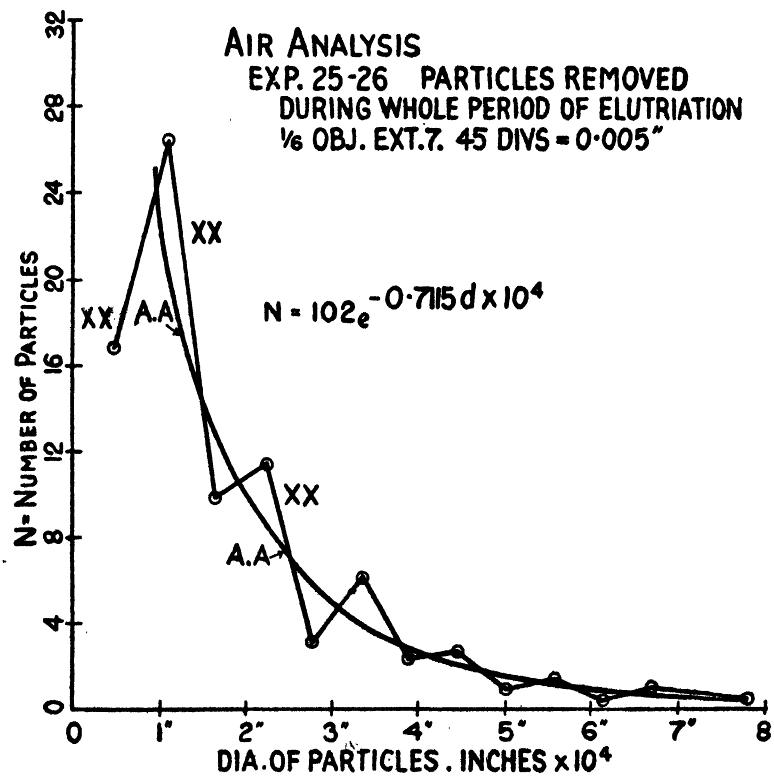

Fig. 3.

is the ratio between successive ordinates for a given unit change in mean diameter. Since $\frac{dN}{dx} = ae^{-bx}$, the total number of particles in the sample of ground sand is $N_0^\infty = \int_0^\infty ae^{-bx}dx = \frac{a}{b}$. Knowing the constants a and b a number of other interesting quantities can be calculated for any given sample of sand. The total number of particles between any two limits of diameter x_1 and x_2 is

$$\frac{a}{b}\left(\frac{1}{e^{bx_1}} - \frac{1}{e^{bx_2}}\right)$$

Deviations from the compound interest law were noted when the fines obtained in the elutriation experiments were examined. A good example is shown in Figure 3, where the points denote the observations and the smooth

curve AA represents the theoretical curve. In all determinations where particles less than 1×10^{-4} inches in mean diameter were being counted, there was a decline in the curve in this region towards the Y-axis. It has been shown that this change in curve is due to the fact that not all the small particles can be counted, and that the shape of the curve in this region depends upon the optical system used for measuring and counting the particles. In Figure 3 the smooth curve is represented by

$$N = 102.0 \times e^{-0.7115d \times 10^4}$$

Where N is the number of particles having the mean diameter d.

To check the closeness with which the experimental data follow the compound interest law, it is sufficient to compare the ratio of successive ordinates for equal changes in abscissa of dx. The law requires that

$$\frac{\frac{dN_1}{dx}}{\frac{dN_2}{dx}} = \frac{\frac{dN_2}{dx}}{\frac{dN_3}{dx}} = \frac{\frac{dN_3}{dx}}{\frac{dN_4}{dx}} = \text{constant}$$

or that

$$\frac{N_1}{N_2} = \frac{N_2}{N_3} = \frac{N_3}{N_4} = \text{constant.}$$

In the 5,000 revolution grinding

$$\frac{dN_1}{dx} \Big/ \frac{dN_2}{dx}$$

was found to be either 1.457 or 1.458 in 20 determinations for particles of mean diameter $4.724 - 18.90 \times 10^{-4}$ inches.

Martin makes the statement that "the law is probably the expression of the fact that crystals have a definite and fixed structure, and consequently break up when subjected to percussion or pressure in the same regular and definite manner all down the scale of magnitude, a definite mathematical law being followed when the number of particles is sufficiently numerous to allow of the application of the law of probability thereto."

II. A Method of Accurately Determining Experimentally the Surface of Crushed Sand Particles.

Martin, with Bowes and Christelow,[1] treated their crushed sand samples with hydrofluoric acid under definite conditions and from the loss in weight of silica calculated the amount of surface of the particles. The crushed sand is first treated with concentrated hydrochloric acid to remove iron (from the iron mill) and soluble matter. After washing and drying a charge of 0.5 to 1 gram of sand is placed in a celluloid or bakelite container. One hundred and fifty cc. of standardized hydrofluoric acid, $1N$ to $5N$, is added and the closed container is attached to a shaking device operating in a water thermostat maintained at 25° C. The charge is shaken at 150 to 200 revolutions per minute for one hour. The container is removed and its contents poured into 100 cc. of ice-cold distilled water. The dilute solution and washings are poured through a Gooch crucible and the ground sand retained on filter paper pulp. The residue is washed, dried, ignited and weighed. The loss in weight of silica has been due to the action of the hydrofluoric acid.

Rectangular blocks of quartz approximately $2.8 \times 1.8 \times 1.0$ cm. were accurately measured and the surface calculated. They were subjected to the

action of $5N$ HF solution for one hour at 25° C., the solution being stirred continuously. The loss in weight was found to be 0.000209 gram per sq. cm. For a 1 N HF solution the loss in weight in one hour at 25° C. amounted to 0.0000418 gram per sq. cm. of surface exposed. Normal acid was used on the coarse sands, and the stronger acid on the fine sands. A 1.0000 gram sample of ground sand treated with normal HF for one hour at 25° C. lost 0.03827 gram, hence the absolute surface of 1 gram of sample is 915.5 sq. cms.

The reaction between silica and hydrofluoric acid takes place in two stages—

$$(1)\quad SiO_2 + 4HF = SiF_4 + 2H_2O$$
$$(2)\quad SiF_4 + 2HF = H_2SiF_6,$$

provided there is an excess of acid present. Under these conditions no hydrolysis occurs and hydrofluosilicic acid is the only product of reaction formed. With the large bulk of liquid used, the concentration of acid remains practically constant, thus maintaining the rate of reaction constant. The rate of stirring was found important, for with slow rates the loss of weight was lower than with high rates of speed. It is assumed that each quartz particle is surrounded by a thin layer of SiF_4 which is in turn surrounded by a saturated layer of hydrofluosilicic acid. It is necessary to maintain the layer of hydrofluosilicic acid as thin as possible in order to have a maximum rate of reaction. A series of experiments indicated that 100 r.p.m. for the shaking gave the maximum rate of loss of weight under the experimental conditions prevailing.

III. Connection Between the Surface Area Produced and the Work Done in Tube-Mill Grinding of Quartz Sand.

Martin, with Bowes and Turner,[1] were able to prove that in the tube-mill grinding of quartz sand, the work expended in grinding is proportional to the surface produced, as stated by von Rittinger. The surface of a ground sample was determined by finding the loss in weight due to solution by hydrofluoric acid as described in Part II. The work expended in grinding was determined by calibrating the 18″ x 18″ tube mill and 2 h-p. motor used in driving it. The total power delivered by the motor armature was determined by measuring the voltage V across the armature and the current C carried in the armature circuit, the total power being CV watts. Loss in the motor due to resistance of parts and by heating was determined by measuring the total circuit resistance R, and from the armature current C, calculated as C^2R watts. Mechanical loss in the motor due to friction losses in the motor was determined by measuring the electrical constants of the motor running without load at different motor speeds, and was checked by a direct power method using a brake. The net power which the motor can deliver to the mill is the armature wattage minus the two losses mentioned.

The friction losses in driving the mill itself without grinding action were then determined for the mill empty and for the mill loaded with blocks of concrete placed concentrically. The losses at various speeds were thus found, and curves plotted to show losses at different speeds and with different loads. The power required to grind the sand is thus the difference between the power delivered to the mill and the power absorbed by the mill due to friction and other losses. In one test 0.85 British h-p. was delivered by the motor to the mill, and 0.28 h-p. absorbed by the mill, leaving 0.57 h-p. to be absorbed in grinding the sand.

In the grinding tests the mill was run at a constant mill speed of 48 r.p.m. with a load of 13.9 lbs. of sand and 247 lbs. of 1″ steel balls. The mill was run

in tests from 600 revolutions to 10,000 revolutions. In the 1,200-revolution test 0.57 h-p. was absorbed in grinding, and this is equivalent to 470,250 ft. lbs. The ground sample lost 0.0252 gram (from 0.500 gram original) in 1 hr. in $1N$ HF acid. The equivalent surface is 589.2 sq. ft. per 1 lb. or 8,190 sq. ft. for a 13.9 lbs. charge. The original sand, 20 to 30 mesh, had a surface of 338 sq. ft. per 13.9 lbs. charge, hence the surface was increased by 7,852 sq. ft. by the work of 470,250 ft. lbs., or an increase of 1 sq. ft. by the work of 59.9 ft. lbs.

Up to 3,000 revolutions of the mill the work required to increase the surface of the sand by 1 sq. ft. averaged 60.9 ft. lbs., that is in ordinary tube mill grinding the surface produced is directly proportional to the work done. Above 3,000 revolutions a greater quantity of work (63.65 at 4,000 and 69.2 at 5,000) was required and it is suggested that the finer particles present act as a cushion, and hamper the crushing of the particles. For greater efficiency in very fine grinding it is essential to remove the dust by an air stream.

IV. On the Air Analysis of Large Quantities of Crushed Sand.

Martin and Watson [1] describe in detail the two kinds of apparatus they built for air-elutriation separation of crushed sand into component grades. One apparatus separated sand particles ranging from a fine dust to 0.2957 mm. in diameter, blown over with an air speed of between 0.18 ft. per sec. and 4.89 ft. per sec. The other apparatus was used for separating the coarser grades of sand ranging from 0.2957 mm. to 1.2 mm. in diameter, blown over with an air speed of between 4.89 ft. per sec. to 20 ft. per sec. Special precautions were taken to have a uniform air flow. The air was heated to dry it and thus prevented the fine dust from sticking to the walls of the elutriating tube. An electrical tapper helped to maintain the tube free of particles. The elutriating tubes were brass tubes, 5 to 6 ft. long, and 2 to 6 in. bore, having at the bottom a cone to hold the sand sample and at the top a collection chamber. A nozzle (3/16 to 7/16 in. bore) was supported vertically downwards just above the sand sample.

Some 20 grades of sand were thus prepared by air elutriation, the grading velocities and the average size of particle in each grade being listed in Table 1.

TABLE 1. *Grading Velocity and Size of Sand Particles.*

Grading Velocity in ft./sec.	Average Size of Particle in mm.	Grading Velocity in ft./sec.	Average Size of Particle in mm.
0.18–0.29	0.0333	1.36– 1.75	0.1089
0.29–0.34	0.0401	1.75– 2.11	0.1305
0.34–0.39	0.0459	2.11– 2.60	0.1551
0.39–0.44	0.0513	2.60– 3.14	0.1803
0.44–0.47	0.0551	3.14– 3.78	0.2172
0.47–0.56	0.0593	3.78– 4.16	0.2587
0.56–0.66	0.0673	4.16– 4.89	0.2957
0.66–1.09	0.0753	7.32– 8.55	0.4853
1.09–1.30	0.0895	9.91–11.32	0.6277
1.30–1.36	0.0928	12.86–14.64	0.8325

Confirmation of the Compound Interest Law for the Distribution of Crushed Sand. In Part I it was shown that log N (the number of particles) when plotted against x (the mean diameter of the particles) gave a straight line representing the compound interest law. As N is proportional to $\frac{W}{x^3}$, where W is the weight of a given graded sample, then plotting log $\frac{W}{x^3}$ against x should

give a straight line. This is found to be true for the grades of varying diameters of crushed sand separated by the air elutriator. Figure 4 shows this relationship graphically, where *W* represents the percentage weight of a grade.

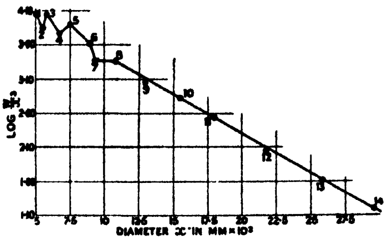

FIG. 4.

V. On the Existence and Preparation of Statistically Homogeneous Grades of Crushed Sand.

Martin with Bowes, Coleman and Littlewood[1] took one of the grades of sand prepared by air elutriation as described in Part IV, and re-elutriated it eight times in order to determine whether any further grading could be obtained. Frequency curves were plotted for each regraded sample, i.e.,

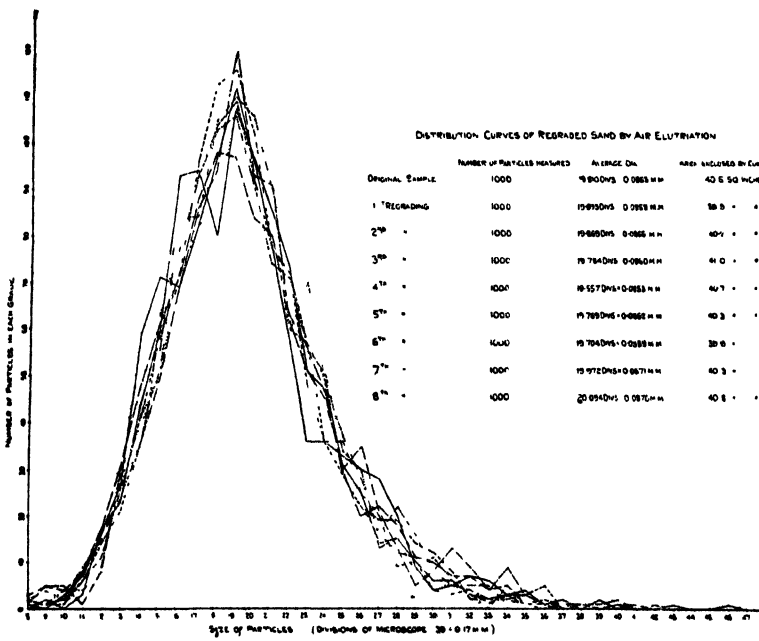

FIG. 5.

number of particles against average diameter. As will be noticed from Figure 5 the frequency curves fall quite close together. The average diameter for each regrading is also given in Table 2. The curves are very much alike in shape and show that there is little or no change in the distribution of the particles caused by continued regrading.

TABLE 2. *Average Particle Size.*

Regrading	Scale Divisions	Mm.
Original grade	19.810	0.0863
1st	19.693	0.0858
2nd	19.869	0.0866
3rd	19.734	0.0860
4th	19.557	0.0853
5th	19.769	0.0862
6th	19.704	0.0859
7th	19.922	0.0871
8th	20.094	0.0876
Average	19.800	0.0863

An average curve obtained from the results of the eight regradings resembles the frequency curve of the original grade quite closely.

It is shown that the frequency curves obtained by plotting number of particles against diameters (see Fig. 5) have the forms of probability curves, the "probability law" being expressed by the equation:—

$N = a\,e^{-bx^2}$, where N is the number of particles, x the diameter, a and b are constants. It is concluded that by careful elutriation crushed sand can be separated into grades which are "statistically homogeneous grades of sand," i.e., these grades elutriate without further grading independent of the number of times the regrading is carried on.

VI. On the Diameters of Irregularly Shaped Crushed Sand Particles Lifted by Air Currents of Different Speeds and Different Temperatures.

Martin[1] made experiments with his air elutriation apparatus to determine the lifting power of air currents at different temperatures and air velocities.

$$V = K\sqrt{d} \quad . \; . \; . \; . \; . \qquad (3)$$

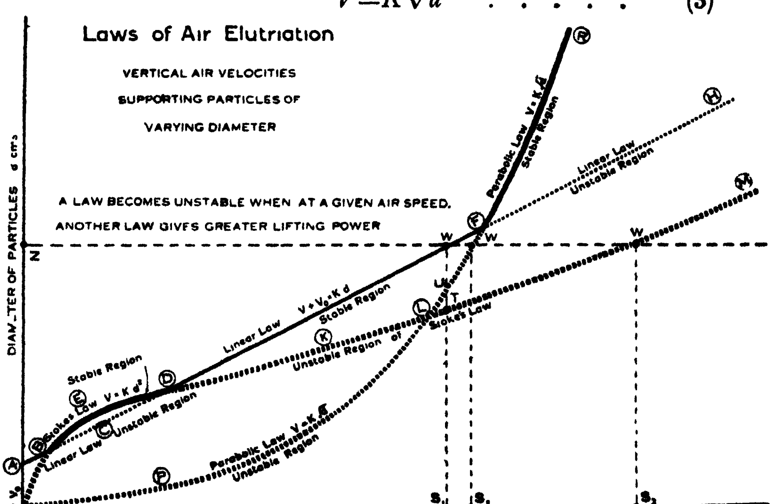

FIG. 6.

Most of the experiments were performed with air in turbulent motion, a few experiments being performed with air in stream-line motion. Martin suggests that the most accurate and rapid method of determining the diameter of

irregularly shaped particles is to estimate the velocity of the fluid which just supports them.

Air in Turbulent Motion.

Working with particles of crushed quartz sand from 1×10^{-1} to 9×10^{-1} cm. in diameter there were found three ranges of diameters, each range following its own law for the relationship between the diameter of the particle and the velocity of air required to lift it. In this paper the diameter d of the particle

TABLE 3. *Application of Laws to Particle Size and Velocities.*

Air Temperature 15.6° C.

Turbulent Motion	Equation	Velocity cms./sec.	Particle Diameter cm.
Law 1. Stokes' Law.	$V = Kd^2$	0.5	0.98×10^{-3}
		25.0	6.91×10^{-3}
	Critical Values	27.5	7.25×10^{-3}
Law 2. Linear Law.	$V + V_0 = Kd$	36.4	8.92×10^{-3}
	(where $V_0 = Kd_0$)	419.0	83.25×10^{-3}
	Critical Values	1081.0	208.00×10^{-3}
Law 3. Square Root Law.	$V = Kd^{1/2}$	1086.0	210.00×10^{-3}
		2245.0	900.00×10^{-3}

EXTENSION OF TABLE 3.

	Velocity of Air cms./sec.	Diameter of Particles mm.	Weight of Particle gms.
Region of Stokes' Law. $V = Kd^2$.	0	0	0
	0.5	0.0098	0.71×10^{-9}
	1.0	0.0138	1.97×10^{-9}
	5.0	0.0309	2.22×10^{-8}
	10.0	0.0437	6.28×10^{-8}
	15.0	0.0535	1.15×10^{-7}
	20.0	0.0618	1.78×10^{-7}
	25.0	0.0691	2.48×10^{-7}
Critical Values	27.5	0.0725	2.87×10^{-7}
Region of Linear Law. $V + V_0 = Kd$.	30.0	0.073	3.47×10^{-7}
	35.0	0.0866	4.88×10^{-7}
	40.54	0.0975	6.98×10^{-7}
	71.78	0.1571	2.92×10^{-6}
	105.45	0.2215	8.04×10^{-6}
	137.9	0.2835	1.172×10^{-5}
	241.8	0.482	8.43×10^{-5}
	323.5	0.638	1.95×10^{-4}
	450.	0.880	5.14×10^{-4}
	500.	0.970	6.98×10^{-4}
	600.	1.167	1.19×10^{-3}
	800.	1.549	2.8×10^{-3}
	1,000.	1.93	5.67×10^{-3}
Critical Values	1,081.	2.08	6.78×10^{-3}
Region of Square Root Law. $V = Kd^{1/2}$.	1,100.	2.16	7.59×10^{-3}
	1,500.	4.01	4.87×10^{-2}
	2,000.	7.13	2.73×10^{-1}
	2,500.	11.15	1.04
	3,000.	16.05	3.11
	5,000.	44.6	66.7
	7,000.	87.4	502.3
	9,000.	144.5	2,227.
	10,000.	178.3	4,266.

is given as the statistical diameter, being the arithmetic mean diameter of 1,000 particles in each case. The velocity V of the air is given in cms. per sec. The laws in simple form are given with the ranges of particle diameters and

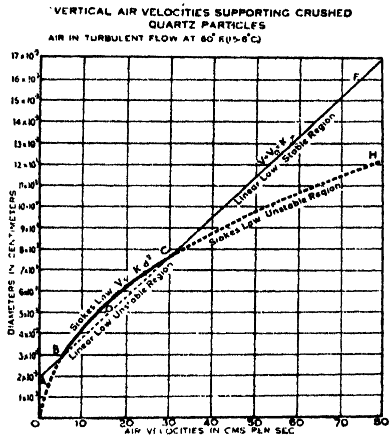

FIG. 7.

velocities they apply to, in Table 3. The numerical values are experimental. The critical values are those which are at the upper limit of values of one law and at the lower limit of another law: they are thus unique in being applicable to two laws. If the curves representing the equations of these laws are plotted,

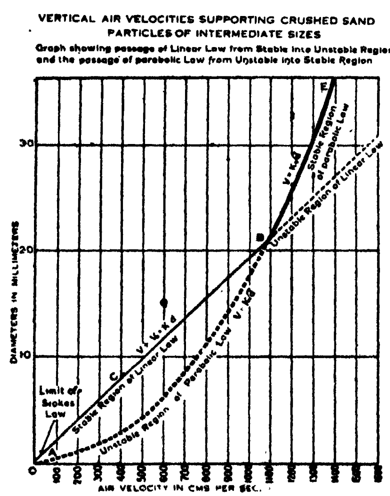

FIG. 8.

the critical values apply to the points where the curves cross each other. Figure 6 gives the three equations in their relative positions, where Law 1 is valid in the region (B) (E) (D), Law 2 is valid in the region (D) (F) and Law 3 in the region (F) (R). In general it may be stated that the law which allows a given particle to be lifted by the least air speed, will be the governing law.

Figure 7 shows the detailed relationship between Laws 1 and 2 with the critical values at *C*, and Figure 8 shows the detailed relationship between Laws 2 and 3 with the critical values at *B*. It should be noted that the curve for the linear equation cuts the ordinate at a positive value, $V_0 = Kd_0$. The other two curves pass through the origin.

Detailed Equations.

Law 1.—Stokes' Law may be stated in the general form

$$V = 0.605k\ (1-h)\ g\left(\frac{s-p}{u}\right) a^2.$$

Experimentally it was found that constants $k = 0.335$ and $h = 0.279$. g is the gravitational constant 981 cms./sec.^{2}, s the specific gravity of quartz 2.65 gms./cm.^{3}, p the density of the moving fluid (air) 1.221×10^{-3} gm./cm.^{3}, u the coefficient of viscosity of the moving fluid 181×10^{-6} c.g.s. units, $a = \frac{1}{2}d$ (diameter in cms.), v the velocity of the air in cms./sec.

Whence $$V = 0.5247 \times 10^6 d^2.$$

or $$d = 1.382 \times 10^{-3}\ (V)^{1/2}$$

Law 2.—Linear Law has the general form of equation

$$V = k\left(\frac{s-p}{p}\right)^{2/3} . g^{2/3} . \frac{a - ha^1}{y^{1/3}}$$

where the coefficient of kinematic viscosity of the moving fluid $y = \frac{u}{p}$, and the other letters have the same significance as given above. The critical radius a^1 of the particles may be calculated from the formula,

$$(a^1)^3 = \frac{9u^2}{2gp\ (s-p)}$$

and denotes the dimension of the largest particle which can be lifted by the air under the given conditions. Combining these relationships Law 2 may be put in the form

$$V = 0.605\ k(a^1 - ha^1)\ g\left(\frac{s-p}{u}\right) a.$$

Applying the constants the equation reduces to $V + V_0 = Kd$

$$V + \left(\frac{2 \times 10^{-3}}{0.19105 \times 10^{-3}}\right) = (0.19105 \times 10^3) d$$

or

$$d = (0.19105 \times 10^{-3})\ V + (2 \times 10^{-3}).$$

Law 3.—Square Root Law has the form

$$V = K\left(\frac{s-p}{p}\right)^{1/2} d^{1/2}$$

Where K is a constant independent of the viscosity of the medium but depending largely upon the shape of the particle. For approximately round shaped grains $K = 4.6$. From Gibbs' [7] work it is deduced that

$$V = 316.2\ K\ (s-p)^{1/2}\ d^{1/2}$$

$$\text{For } K = 4.6,\ s = 2.65 \text{ and } p = 1.221 \times 10^{-3}$$

$V = 2371\ d^2$, for quartz in the fluid medium—air, V being measured in cms./sec. and d in cms.

Influence of Temperature of the Air in Turbulent Flow—for Law 2, Linear Law.

Influence of temperature for the linear law was obtained by calculation only. In the general equation $V + V_0 = Kd$, $V_0 = Kd_0$—a constant velocity,

$$V_0 = \frac{0.605\ khsg\ (a^1)^2}{u}$$

and

$$V = \frac{(0.605\ ksga^1)}{u}\,a - V_0$$

or

$$a = \frac{(V + V_0)u}{0.605\ ksga^1}$$

a^1 the critical radius of the particle being calculated from the formula

$$(a^1)^3 = \frac{9u^2}{2\,gsp}$$

u can be calculated for any gas at any temperature from Sutherland's Law. For air a few values are given in Table 4.

TABLE 4. *Values for Air.*

t °C.	u	p	a^1	V_0
15.6	181×10^{-6}	12.21×10^{-4}	3.6×10^{-3}	10.53
100	224	9.47	4.5	13.29
501	361	4.56	7.9	25.42
1093	509	2.59	12.0	41.59
1427	579	2.08	14.1	50.46

The general effect of raising the temperature of the air is to increase the carrying capacity of the air, as may be noted from the increase in a^1, the velocity V of the air being constant for these comparisons.

Air in Stream-Line Flow.

It was experimentally demonstrated that for a given velocity of air, the air in the stream-line state had greater lifting power than air in the turbulent state. The linear law (Law 2) was found to hold with the constants $k = 0.2073$ and $h = 0.1667$, for particles between 3.33×10^{-3} cm. diameter (velocity observed 7.2 cm./sec.) and 6.73×10^{-3} cm. (velocity 18.6 cm./sec.), the air being at room temperature.

VII. On the Efficiency of Grinding Machines and Grinding Media with Special Reference to Ball and Tube Mills.

Martin, with Turner and Linstead,[1] continued the work on grinding efficiency described in Parts II and III. The formula $W = B(S_2 - S_1)$ holds for grinding when not carried beyond 3,000 revolutions under the conditions of test. W is the work in ft. lbs., S_2—the surface of powder after grinding, S_1—the surface of powder before grinding, B a constant dependent upon the grinding medium, the material, the type of mill. B expresses the work required to increase the surface by one sq. ft.

An experiment was conducted to determine the difference in efficiency of

grinding between 1 in. steel balls and ¾ in. steel balls. 13.9 lbs. of sand was ground with 247 lbs. of steel balls in an 18 × 18 in. experimental mill varying the time of grinding and determining the work involved in each case. From 600 to 3,000 revolutions of the mill, 60.9 ft. lbs. of work were required by the 1 in. steel balls and 44.8 ft. lbs. by the ¾ in. steel balls to increase the surface of the sand by 1 sq. ft. Another conclusion reached was that when the increase of surface had exceeded fivefold the original surface, the efficiency fell off rapidly, the sand particles being then too fine for the size of the balls. A general policy to follow for obtaining high efficiency is to maintain the surface of the powder in the mills between 100 and 500 times the surface of the balls.

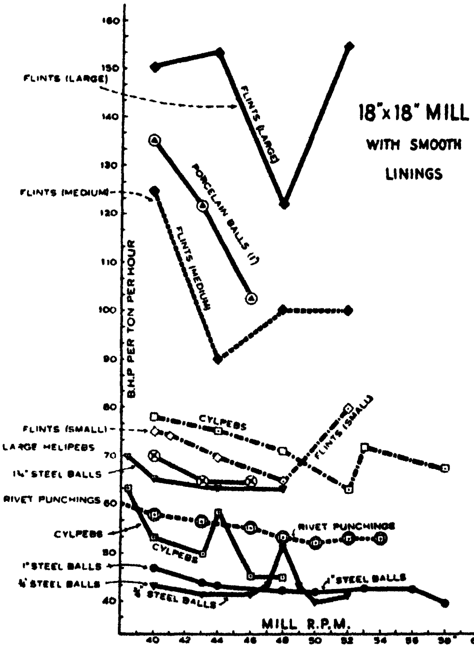

DIAGRAM REPRESENTING B.H.P PER TON PER HOUR REQUIRED TO GRIND STANDARD LEIGHTON BUZZARD SAND TO 5% RESIDUE ON 180 CEMENT SIEVE USING DIFFERENT GRINDING MEDIA

FIG. 9.

Another series of experiments was run on the 18 × 18 in. tube mill to compare the grinding efficiency of different kinds of grinding media. Sand was ground until the residue on a 180 mesh sieve was 5 per cent by weight, and the required B.h-p. (British horse power) was determined. Figure 9 shows the results calculated to B.h-p. per long ton. Steel balls and shapes grind faster than flints or porcelain balls. The best mill speed was found to be $N = \frac{200}{(d)^{1/2}}$, where N = r.p.m. of a mill and d inches in internal diameter. No difference in best mill speed or in efficiency at best mill speed was found between a tube mill 18 × 18 in. and a tube mill 72 × 30 in., when 1 in. steel balls were used. The ball load is recommended to occupy between 30 and 40 per cent of the apparent mill volume.

VIII. On the Variation in the Specific Gravity of Quartz Sands on Prolonged Grinding.

Martin, with Watson and Bowes,[1] determined the effect of grinding on the specific gravity of quartz, using the "vacuum pycnometer" described by Washburn and Navias.[6] Specific gravities at 15° C. referred to water at 4° C. are:— standard sand 2.650, ground 25 to 50 min. 2.653, ground 3.5 hrs. 2.649. If the lowering in specific gravity is due to the formation of amorphous silica, the conversion on the 3.5 hours grinding amounts to 0.91 per cent. The amorphous silica seemed to be chiefly formed among the fine particles, especially less than 0.03 mm. in diameter.*

IX. Connection between the Statistical Diameter and the Statistical Volume of Irregularly Shaped Particles of Crushed Sand.

Martin and Bowes[1] worked on this phase of research. The statistical diameter of an irregularly shaped particle is the linear dimension across the particle, when the line along which the reading is taken divides the particle into two equal areas and for a given particle it may vary with the direction along which the reading is taken. The average statistical diameter d is obtained by measuring a number of particles and finding the arithmetic mean. The statistical volume V is obtained by measuring the actual total volume of a large number of particles and calculating the average volume of a single particle.

The relationship between V and d^3 was studied by following the ratio $\frac{V}{d^3} = B$, where B is known as the "volume constant" of the powder. For a set of cubes of uniform side d, and volume V, $V = 1d^3$, hence $B = 1$. The statistical diameter of a cube of side d is $1.122d$, hence

$$V = B\,(1.122d)^3, \quad \text{and} \quad B = 0.7082.$$

For spheres

$$V = \frac{\pi}{6}d^3 \quad \text{and} \quad B = \frac{\pi}{6} = 0.5236.$$

For the irregularly shaped quartz grains five carefully graded air-elutriated samples were chosen. In each grade were measured the numbers n_1, n_2, n_3 . . . of particles having diameters, d_1, d_2, d_3 . . . in a definite weight of sample, having a total number of particles N. Then $N = n_1 + n_2 + n_3 + \ldots$ and $V = B(n_1d_1^3 + n_2d_2^3 + n_3d_3^3 + \ldots)$, where it is assumed that B is a constant over the narrow range. 1,000 particles of each grade were measured, and it is assumed that this number is large enough to give an accurate representation of the distribution. From the determinations of n_1, d_1, N and V, B was calculated for each grade. Results are given in Table 5.

TABLE 5.

Mean Diameter of Grades Cm.	No. of Particles per Gm. (by count)	Volume Constant B
0.02172	116,520	0.275
0.02587	68,120	0.283
0.02957	47,200	0.273
0.03582	27,200	0.271
0.08328	2,188	0.284
	Mean value	0.277

* *See* paper by L. Navias in this volume under heading "The Effect of Prolonged Grinding on the Density of Quartz."

From these results it may be concluded that the volume constant B is essentially a constant for the range of diameters considered and hence the average shape of sand particle remains the same over this range.

X. On the Connection between the Statistical Diameter of Crushed Sand Particles and Their Statistical Surface.

Martin and Bowes [1] extended their consideration to the relationship between statistical diameter d and statistical surface S. The statistical surface was measured for 19 closely graded air-elutriated ranges of crushed quartz sand by the hydrofluoric acid method. The total surface of a large number of particles divided by the number of particles gives the statistical surface S. The relationship $\frac{S}{d^2} = A$, was found to hold, A being the "surface constant." For a cube the relationship is $S = 6d^2$, where $A = 6$, and d is the length of a side. For a sphere $S = 3.1416d^2$, where $A = 3.1416$ and d is the diameter. For each grade of crushed quartz sand the number of particles in 1 gram of sample, $x_1, x_2, x_3 \ldots$ having diameters $d_1, d_2, d_3 \ldots$ were determined by the microscope. Then from

$$S = A\ (x_1d_1^2 + x_2d_2^2 + x_3d_3^2 + \ldots\ldots..)$$

where S is the determined surface of 1 gram charge, A was calculated. The surface constant varies between 1.95 to 2.49, as will be noted from Table 6. On the whole the average shape of the sand particles remains the same on crushing from 0.08 cm. diameter to 0.003 cm.

TABLE 6.

Mean Diameter of Grade Cm.	No. of Particles per Gm.	Absolute Surface per Gm. Sq. Cms.	Surface Constant A
0.00333	31,426,800	791	2.14
0.00401	16,705,650	584	2.01
0.00459	11,296,900	508	1.98
0.00513	8,486,100	496	2.10
0.00551	7,181,850	443	1.95
0.00593	5,676,650	414	1.98
0.00673	3,846,150	367	2.01
0.00753	2,779,800	334	2.03
0.00895	1,650,000	315	2.27
0.00928	1,469,030	292	2.20
0.01089	889,050	244	2.21
0.01305	522,300	221	2.35
0.01551	323,300	187	2.29
0.01803	202,900	162	2.35
0.02172	116,520	141	2.44
0.02587	68,120	118	2.48
0.02957	47,200	107	2.49
0.04853	27,200	68.2	2.49
0.06277	——	52.7	2.49
0.08325	2,188	39.7	2.49

XI. Calculations Relating to Diameters, Surfaces, and Weights of Homogeneous Grades of Crushed Quartz Sand.

Martin [1] has calculated the surface of a number of his closely graded air-elutriated crushed quartz sand particles from the data mentioned in previous

sections of this series and compares the calculated areas with the observed areas determined by the hydrofluoric acid treatment. The calculated areas are obtained as follows:

$V = NBd^3$, where V is the total volume in cc. of N particles, whose statistical diameter is d. B is the "volume constant." $S = NAd^2$ where S is the total surface of N particles with statistical diameter d, and surface constant A. In place of V may be put $\frac{W}{s}$, where W is the total weight in grams of the N particles having a specific gravity s.

From the two equations $\frac{W}{s} = NBd^3$ and $S = NAd^2$, N may be eliminated and $S = \frac{A}{B} \cdot \frac{W}{s.d.}$ This equation gives the relationship between the surface S and the weight W of particles of a homogeneous grade, A, B, s and d being constants. The relationship was checked by calculating the surface of 1 gram of crushed sand and comparing it with the observed surface. Data are given to show that the correspondence is fair, the calculated surface in all cases being the larger (Table 7).

TABLE 7.

Mean Diameter of Grade Cms.	Surface of 1 Gram S in Sq. Cms. Experimental	S in Sq. Cms. Calculated
0.00333	791	866
0.00401	584	674
0.00459	508	580
0.00513	496	551
0.00551	443	476
0.00593	414	449
0.00673	367	402
0.00753	334	363
0.00895	315	341
0.00928	292	319
0.01089	244	273
0.01305	221	243
0.01551	187	199
0.01803	162	173
0.02172	141	151
0.02587	118	128
0.02957	107	113
0.09237	24.29	24.26

Work of Gross and Zimmerley.[2]

Crushing and Grinding.[3, 4, 5]

Surface Measurement of Quartz Particles.—Gross and Zimmerley used a "dissolution method" for the determination of surface of ground quartz by noting the initial rate of dissolution in hydrofluoric acid. They argue that as the quartz particles are dissolved, the reaction velocity changes, due to a change in concentration of the solution and due to a change in surface of the solid. By plotting the rate of dissolution for various periods of time, a curve is obtained which, if extrapolated to the zero time ordinate, gives the initial rate of dissolution at zero time. This is a measure of the amount of surface involved.

The sample should be large enough to yield 50 mg. of dissolved quartz in 1 hour, as for instance 1-gram sample for fine materials and a 16-gram sample for coarser materials. The ground quartz enclosed in a bakelite tube with hydrofluoric acid is agitated by rotating the tube end over end at 20 r.p.m. in a thermostat held at 25° C., for periods of ½ hr. to 2 hrs. The concentration of acid used was 3.66 *N*, or 73.2 grams HF per liter. The volume of solution varied between 25 cc. and 250 cc. The quartz particles remaining in the solution are removed by a vacuum filtration and washed free of acid. Ignition loss of the sample is taken into account.

From the experimental data two curves are drawn: (1) cumulative curve of per cent quartz dissolved plotted against time, the curve passing through the origin; (2) the rate curve of per cent quartz dissolved per hour plotted against time. The extrapolation of the rate curve to the zero time ordinate gives the initial rate (I.R.). Mathematical expressions were found for both curves:

$$R = \frac{A + at}{1 + Kt}, \quad \text{and} \quad C = \frac{At + at^2}{1 + Kt}$$

in which R is the per cent quartz dissolved per hour; C, per cent quartz dissolved; A, initial rate; a, a constant; K, a constant; t, the time in hours.

It was found that quartz crystals are dissolved by hydrofluoric acid in the direction of the vertical axis. Comparison of dissolution rates of massive quartz, Ottawa quartz sand and a large quartz crystal, each being crushed to the same particle size, namely, a 100 to 150 mesh product, showed that the initial rate was the same for each kind.

Accuracy of within 5 per cent of the true value is claimed for this method provided precautions are taken to obtain a representative sample and to correct for loss in handling of fine particles and for ignition loss. Where very fine particles are involved, dilute acid solutions must be used. In this work it is assumed that Wenzel's law holds, namely, that "the reaction velocity between solids and liquids is proportional to the area of contact." A factor, 170, was determined whereby the I.R. values could be converted into sq. cms. of surface per gram of quartz. Ottawa sand and quartz crystals were dipped into a silvering solution for 30 minutes. From the determined area of surface of the quartz crystals and the weight of silver picked up, the weight of silver deposited per unit area of surface was calculated and these values applied to the spherically shaped Ottawa sand particles. Data for these sand particles are given in Table 8. The authors state that the I.R values accurately express surface and give true comparisons of surface, whereas the silver-coating method is approximate and used only as a convenience.

TABLE 8. *Surface Measurements of Ottawa Sand by Silver Coating.*

Screen Limits Sieve Nos.	Surface Sq. Cm. per Gm. as Determined by Silver Coating	Theoretical Surface Cubes or Spheres, Sq. Cm. per Gm.	Ratio of Measured to Theoretical Surface	Initial Rate (I.R.)	Factor to Convert I.R. to Sq. Cm. per Gm.
28–35	60.97	45	1.355	0.358	170.3
35–48	83.64	63.5	1.317	0.497	168.3
48–65	118.23	90	1.314	0.732	161.5
65–100	176.40	127	1.389	1.020	172.9
100–150	249.95	180	1.389	1.389	180.3
150–200	338.72	254	1.334	1.923	176.1

The Relation of Measured Surface of Crushed Quartz to Sieve Sizes.— Gross and Zimmerley [2] crushed quartz to pass a 20-mesh screen. The fines were separated by wet screening on a 270-mesh sieve. After drying the coarser material was sieved by hand into a number of classes as shown in Table 9. Tyler standard sieves were used. The "average size" of particle of a sieve-sized product was taken as the mean of the limiting sieve sizes, and is given in the second column. For each "average size" was calculated the theoretical surface per gram of quartz, considering each particle as a sphere with diameter equal to the "average size," or as a cube with side equal to the "average size" in dimension.

By means of the "dissolution method" the initial rate (I.R.) of solution in hydrofluoric acid was determined for each sieve-sized product. The equivalent measured surface in sq. cms. per gram was calculated. In the last column is given the ratio between the measured and theoretical surface, and it should be noted that this ratio is much higher for the coarser particles than for the finer particles.

To test the reliability of the dissolution method, Ottawa sand, whose grains are nearly spherical, was graded by sieving and treated in a similar manner.

TABLE 9. *Data on Sieve Sizes of Crushed Quartz.*

Screen Limits Sieve Nos.	Average Size of Particle, Mm.	Theoretical Surface per Gram of Quartz Cubes or Spheres, Sq. Cm.	Initial Rate (I.R.)	Measured Surface per Gram, Sq. Cm. I.R.×170	Ratio of Measured to Theoretical Surface
3–4	5.690	4.0	0.201	34.2	8.55
4–6	4.013	5.65	0.258	43.9	7.77
6–8	2.845	8.0	0.307	52.2	6.53
8–10	2.007	11.3	0.351	59.7	5.28
10–14	1.410	16.0	0.425	72.3	4.52
14–20	1.001	22.5	0.525	89.3	3.97
20–28	0.711	31.8	0.632	107.4	3.38
28–35	0.503	45.0	0.823	139.9	3.11
35–48	0.356	63.5	1.038	176.5	2.78
48–65	0.252	90.0	1.393	236.8	2.63
65–100	0.178	127.0	1.851	314.7	2.48
100–150	0.126	180.0	2.504	425.7	2.37
150–200	0.089	254.0	3.219	547.2	2.15
200–270	0.063	360.0	4.287	728.8	2.02

In Table 10 are given the results and it is seen that the ratio of measured to theoretical surface is fairly constant, and that the measured values are only slightly greater than the theoretical. By plotting the logarithm of measured surface (sq. cms. per gram) against the logarithm of average particle size (in microns), a straight line is obtained for theoretical cubes or spheres, ending at the ultimate particle—the unit quartz crystal, whose average dimension is 0.0005 micron. 1 gram of such unit crystals has a calculated surface of 66.5×10^6 sq. cms. The curve for the Ottawa sand is also a straight line lying close to the theoretical curve, whereas the curve for the crushed quartz shows some curvature.

The greater measured surface, especially in the coarser quartz particles, is attributed to (1) a change of shape in the particles and (2) cracks in the particles, which may be seen under the microscope, and noted also by the

manner in which HF acid enters the cracks and splits up the particles. To determine the amount of surface in these cracks, the surface of the particles was determined by the HF dissolution method and by the silver-coating method. As the silver does not penetrate the cracks, the silver-coating method measures the exterior surface only. Table 11 gives the data, and shows that

TABLE 10. *Data on Sieve Sizes of Ottawa Sand.*

Screen Limits Sieve Nos.	Average Size of Particle, Mm.	Theoretical Surface per Gram of Quartz Spheres, Sq. Cm.	Initial Rate (I.R.)	Measured Surface per Gram, Sq. Cm. I.R.×170	Ratio of Measured to Theoretical Surface
20–28	0.711	31.8	0.255	43.4	1.37
28–35	0.503	45.0	0.358	60.9	1.35
35–48	0.356	63.5	0.497	84.5	1.33
48–65	0.252	90.0	0.732	124.4	1.38
65–100	0.178	127.0	1.020	173.4	1.37
100–150	0.126	180.0	1.386	235.6	1.31
150–200	0.089	254.0	1.923	326.9	1.29

TABLE 11. *Data on Surface Measurements of Crushed Quartz by Dissolution and by Silver Coating.*

Screen Limits Sieve Nos.	Theoretical Surface per Gram of Quartz Cubes or Spheres, Sq. Cm.	By Dissolution: Measured Surface Sq. Cm. per Gram	By Dissolution: Ratio of Measured to Theoretical Surface	By Silver Coating: Measured Surface Sq. Cm. per Gram	By Silver Coating: Ratio of Measured to Theoretical Surface	Ratio of Interior to Outer Surface
3–4	4	34.2	8.55	9.4	2.35	2.638
6–8	8	52.2	6.53	18.6	2.33	1.807
10–14	16	72.3	4.52	36.0	2.25	1.008
20–28	31.8	107.4	3.38	59.1	1.86	0.817
35–48	63.5	176.5	2.78	122.1	1.92	0.446
65–100	127	314.7	2.48	252.9	1.99	0.244
150–200	254	547.2	2.15	493.0	1.94	0.110

in the larger particles the greater part of the surface resides in the cracks. From the results obtained by the silver-coating method it is shown that the shape of the particles remains essentially the same for both large and small particles.

From measurements by the dissolution method it was found that quartz particles passing through a 200-mesh screen had a smaller average diameter than 37 microns, the generally accepted figure; 37 microns being the average of 74-micron opening for the 200-mesh sieve and 0. The measurements found for quartz varied between 5 and 18 microns, indicating a rather large amount of fine particles produced in grinding. Much of the work in crushing and grinding is expended in producing finer material than is required.

Relation of Work Input to Surface Produced in Crushing Quartz.—Gross and Zimmerley [2] devised a method and apparatus whereby the work required to crush quartz particles could be measured. The quartz sample was placed in a steel cylindrical mortar with steel plunger in position, and crushed by means of a steel ball falling onto the plunger. The weight of the ball varied from 1.360 to 2.935 kgs., and the maximum fall was 60 cms. The work applied to the plunger is calculated in kg. cms. The mortar rests on 3 aluminum wires, each 1 cm. long and 3.232 mm. in diameter, which in turn lie on a heavy metal

TABLE 12. *Data on Quartz Crushing Tests.*

Exp. No.	Sieve Nos. Sieve Size of Quartz before Crushing	Grams Crushed Each Crushing	Grams Crushed for Dissolution Tests	Crushing Chamber Diam. × Ht.	Data on Work in Crushing					Surface per Gram Sq. Cm. (I. R. × 170)			Surface Produced Sq. Cm. per Kg.-cm.
					Weight of Ball, Kg.	Drop, Cm.	Total Kg.-cm. per Gram	Net Kg.-cm. per Gram to Crushing	Per Cent of Work, Input to Crushing	Crushed Product	Before Crushing	Net Due to Crushing	
A	10–14	12	72	1½″ × ¾″	2.050	20	3.42	3.02	88.4	129.7	72.3	57.4	19.0
B	10–14	4	64	1 × ½	2.050	20	10.25	9.21	89.9	227.1	72.3	154.8	16.8
C	10–14	4	20	1 × ½	2.050	20	10.25	9.37	91.4	249.6	72.3	177.3	18.9
D	35–48	4	80	1 × ½	2.050	30	15.37	10.64	69.2	393.4	200.4	193.0	18.1
E	35–48	4	40	1 × ½	2.935	20.95	15.37	10.64	69.2	400.0	200.4	199.6	18.8
F	35–48	4	72	1 × ½	1.360	45.22	15.37	10.82	70.4	406.5	200.4	206.1	19.0
G	10–14	4	48	1 × ½	2.050	20 + 20	20.50	14.77	72.1	328.1	72.3	255.8	17.3
H	20–28	4	32	1 × ½	2.050	40	20.50	14.79	72.1	349.2	97.4	251.8	17.0
I	20–28	4	{296 g. sized}	1 × ½	2.050	40	20.50	15.04	73.4	340.3	97.4	242.9	16.2
J	10–14	4	56	1 × ½	2.050	40	20.50	16.12	78.6	343.1	72.3	270.8	16.8
K	65–100	3	{108 g. sized}	1 × ½	2.050	50	34.17	19.85	58.1	690.2	369.8	320.4	16.1
L	10–14	4	96	1 × ½	2.050	40 + 40	41.00	25.43	62.0	518.2	72.3	445.9	17.5
M	3–4	2	16	1½ × ¾	2.935	40	58.70	46.45	79.1	878.4	34.2	844.2	18.2
								206.15				3620.0	17.56

base. The aluminum wires are placed radially and are easily deformed. The work applied to the plunger by the falling ball is expended in crushing the quartz particles and in deforming the wires, there being no rebound to the ball. The wires were deformed with varying loads and the deformation plotted against load to give a calibration curve for the wires. Knowing the work applied to the plunger and the work absorbed by the deformation of the wires, the difference is the work consumed in crushing the quartz particles.

As the crushed quartz sample coming from the mortar consists of many sizes of particles, it was desirable to determine whether the "HF dissolution method" could be applied to the sample without sizing by means of sieves or elutriation process. Composite samples were prepared from previously measured sieve-sized and elutriated material, and the surface measured on the composite samples. The results checked quite closely, hence it was found convenient to determine the surface of the crushings directly. Dust loss during the crushings is minimized by moistening the charge with absolute alcohol, and the dust lost is taken into account in the results.

Data for 13 crushing experiments are given in Table 12. Surface per gram of material was determined for each sample before and after crushing. The net increase in surface produced per gram of material was divided by the work (in kg. cms. per gram), yielding an average figure of 17.56 sq. cm. produced by the application of 1 kg. cm. of work. Plotting work input against surface produced per gram of quartz yields a straight line, the relationship being proof of Rittinger's law that "The work of crushing is directly proportional to the new surface produced."

Assuming that the surface energy of quartz is the minimum work theoretically necessary to produce a unit of surface by crushing, it is found that the efficiency of grinding is very low. Using Edser's value of 920 ergs per sq. cm., the efficiency is only 3 per cent for 17.56 sq. cm. yield of surface for 1 kg. cm. of work. Using Martin's value of 310 ergs per sq. cm. the efficiency is only 1 per cent. Martin calculated from his own work that the efficiency of ball mill grinding was only $1/16$ of 1 per cent.

From experiment *I*, starting with 20 to 28-mesh quartz, it was calculated that 73.7 per cent of the work was utilized in producing particles which passed through a 200-mesh sieve. In experiment *K*, starting with 65 to 100-mesh quartz, it was found that 95.3 per cent of the work was spent in producing particles finer than 200 mesh, indicating that the major part of the work consumed in crushing was expended in producing fine material.

Gross and Zimmerley [8] have also described "A Device for Determining Work Input to a Laboratory Mill," measuring the work input at the mill itself, by adapting Haultain's [9] device originated for measuring work input to rolls.

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Colloid Mills and Comminution Chemistry *

By Dr. August Chwala, Vienna.

To reduce various materials to an extremely fine state of subdivision by a cheap and simple method, is of great technical and industrial importance. The colloid mill of Plauson,[1] which appeared about a decade ago, was supposed to have solved this problem. Many years prior to this P. P. von Weimarn [2] had made laboratory experiments in producing fine dispersions by mechanical methods.

The colloid mill did not, however, come up to the extravagant expectations of its makers. Gradually impartial criticism arose, based on an examination, by dispersoid-analytical methods, of the products of colloid mills.[3] It became evident that colloid mills could not produce from solid non-gels the desired colloidal dispersions. Improvements in mechanical construction as well as experiments involving the addition of deflocculators (dispergators) to the material being ground, led to further disappointment. On the other hand these efforts served to direct attention to the heretofore neglected field of *turbid dispersions,* systems intermediate between suspensions and true colloidal solutions. These systems are of particular industrial importance; for while in numberless instances suspensions are too coarse for use, for many technical purposes true colloidal dispersions are also unsuitable because of the peculiar physico-chemical properties exhibited by the extremely fine colloid particles. Just to mention one instance from among the many industries involved: Pigments must, of course, be very finely ground; but if their particle size goes below a certain minimum, they lose in covering power.

In his paper on "Comminution Chemistry," [4] Chwala has discussed the causes underlying certain failures of colloid mills, and has pointed out that the previously forgotten and overlooked *solid non-gels* could not be converted into colloidal systems by mechanical methods alone, nor by a combined chemico-mechanical treatment. The problem posed by the author in the title of this paper (comminution chemistry) envisages the peptization or dispersion, with or without mechanical aid, of solid non-gels which are essentially difficult to peptize or disperse, whereby there arise new physico-chemical properties not inherent in the original substance. The peptizers or dispergators employed may hardly be said to alter chemically the solid non-gel which is being comminuted; the dispersion is, rather, based upon specific chemical surface reactions.

For the peptization of solid substances (the expression "peptization" is used by different authors to denote different processes), Chwala suggested the following extension of von Weimarn's † formulation: [5]

1. The disperse phase must consist of particles so fine that their physical properties are functions of the particle size.
2. The peptizer must be able, upon sufficient concentration, to form a soluble, stable, chemical *complex,* or something oriented like such a complex.
3. The dispersion medium in which the peptization is to take place, must, in the absence of the peptizer, be practically unable to dissolve molecularly the substance to be dispersed.

* Translated by Jerome Alexander.
† *See* paper by P. P. von Weimarn in Vol. I of this series.—J. A.

4. The particles must be able to attach adsorption layers (solvation shells) about themselves.
5. Kinetic activity acts in all cases as a factor making for stability of the colloidal solution, even though it be subsidiary to other factors influencing the formation or stability of colloids.
6. With most inorganic aqueous colloids, electric charge on the particles is a *conditio sine qua non* (electrokratic sols).

This newly outlined theory of peptization, which envisages von Weimarn's widely known views and experimental results, and which gives a complete explanation of peptization, makes evident why solid non-gels do not yield colloidal systems, and therefore why colloid mills must fail in certain cases. For practically all intending users of colloid mills had mainly in mind (if we except the speeding up of reactions, homogenization, or intimate mixture) such substances as phosphate rock, sulfur, graphite, carbon, ores, iron, etc., that is, substances not only quite insoluble in water, but also insoluble substances which are *not hydrated or solvated*—in other words, solid non-gels *which do not satisfy condition (4) mentioned above.*

These views are supported by the results of a series of experiments made by Chwala, using a large number of solid non-gels and of all kinds of peptizers—in no case did a true colloidal solution form. But in many instances there formed *cloudy dispersions.**

Dispersion of a gel in a fluid medium, according to Chwala's views, may follow substantially the following five steps: There form (1) a suspension; (2) a cloudy dispersion; (3) a colloid; (4) a complex, or (5) a molecular solution in the orthodox sense. If the substance being dispersed be a solid non-gel, the true colloid state is not reached. Of these five stages, the second is least known. They may arise in part successively, in part simultaneously; they are not always easy to separate, for they have no sharp lines of demarcation.

Cloudy dispersions (turbidities), following Zsigmondy,[6] are heterodisperse, thermodynamically unstable colloidal or pseudo-colloidal systems, which exhibit a whole series of properties of true colloids, e.g. Brownian motion, faint Tyndall phenomenon, flocculation by electrolytes, cataphoresis, etc., but which, for example, are not clear, but appear milky to transmitted light. Certainly they contain particles which no longer belong to the colloidal zone. Cloudy dispersions are distinguished from suspensions by the fact that a considerable percentage of their particles are of colloidal, or approximately colloidal, dimensions. Technically they are interesting, important, and common. Thus clay, when dispersed in water, generally does not yield a colloid, but rather a cloudy dispersion, which may be submitted to electro-osmosis and worked up or used in various ways. Cloudy dispersions are important in ore flotation,[7] in the enamel, lacquer, japan, and paint industries, in chemically prepared papers (carbon papers) and in papers generally.

Despite their metastability, these systems well serve technical purposes, for they change into the stable flocculated state at whatever rate is demanded by various manufacturing methods. Apart from sedimentation, cloudy dispersions are further characterized by:[8] particle size, wettability (interfaces, surface tension), relative density of the individual particle, electric charge, filtration limits, diversity in particle structure.

Peptizers generally known in the literature exert no appreciable action on solid non-gels; but Chwala found that sodium pyrophosphate is a most interest-

* The expression "cloudy dispersion" or "turbidity" (the German word is "Trübung," an intermediate stage between colloids and true suspensions), was first used by G. Quincke in Drude's *Ann. Physik.*, 4, 7-57-69 (1902).

ing peptizer for this group of substances, with which it forms turbidities intermediate between suspensions and colloids. Potassium citrate serves the same purpose, but is considerably less efficient.* In the case of pyrophosphate we obviously have an unsymmetrical, deformable (dipolar) molecule, capable of orientation, of forming complexes, and also films (emulsifying power). A relation may exist between the forces which, in pyrophosphate, lead to complex formation, and those forces producing film formation; and a transition may exist between these different forces active at the surface of the dispersed substance.

The author has established the following roughly quantitative differentiation between turbidities and suspensions, which will serve as a good technical guide, though not founded on basic differences: (a) The sedimentation curves shown in the Wiegner-Gessner apparatus † show that with suspensions complete sedimentation occurs in relatively few hours, whereas turbidities had not

TABLE 1.

Material	Calcined Sodium Pyrophosphate	Dry content[a] of the 1 Per Cent Suspension in Distilled Water after Standing 16 Hours
	Per Cent	
1. Lixiviated chalk (brand H)	12	40.
2. Kaolin (brand C.W.)	9	42.
3. Phosphate rock, Gafsa, sifted	9	42.[b]
4. High-grade lime (brand H)	9	40.[b]
5. Carbon black (brand K. & E.)	5	67.5[c]
6. Blanc fixe (brand B, Mannheim)	9	87.[d]
7. Blanc fixe, previously washed	9	90.[d]
8. Blanc fixe (French)	9	89.[d]
9. Barytes (brand S.)	9	32.[d]
10. Calcium arsenate (brand T.S.)	12	60.[e]
11. Calcium arsenate (brand 100)	12	75.[e]
12. Basic copper carbonate (type V_4/b)	9	56.[f]
13. $BaSO_4$ paste (freshly ppted., 40% dry)	0[g]	0.
	1[h]	23.5[i]
	2[h]	27.[i]
	6[h]	35.6[i]
	20[h]	69.5[i]
	50[h]	98.5[i]

(a) This includes any contained sodium pyrophosphate.
(b) After standing 3 hours.
(c) One per cent of a wetting-out agent used.
(d) After standing ½ hour.
(e) Different varieties of calcium arsenate, prepared by different wet methods.
(f) Basic copper carbonate, prepared by the wet method.
(g) 20 grams of the barium sulfate paste was lightly rubbed up in a mortar, and 3 grams of this was weighed into a 300 cc. graduated cylinder. After filling to the mark and then shaking vigorously, the suspension was allowed to stand quietly 16 hours.
(h) 100 grams of the 40 per cent Ba_2SO_4 paste was added to the respective quantities of dry sodium pyrophosphate in a mortar, and lightly rubbed up for several minutes. Three grams of the mixture was weighed into the graduated cylinder for test as above.
(i) Estimated on the basis of the dry material originally present in the 3 grams of mixture.

* Among the great number of substances which were tried, with little or no success, as peptizers for making cloudy dispersions from different pigments, the following may be mentioned: potassium ferrocyanide, sebacic acid, anthracene-2-sulfo-acid, phenylthioglycolarsenious acid, amino 4-oxyphenylarsenious acid, and the Na salts of tannic acid, sodium thiosulfate, hydrazine hydrate. Better results, though not equal to those with sodium pyrophosphate, were had from: potassium sodium tartrate, and the Na salts of salicylic acid, gallic acid, deoxycholic acid, sodium silicate. [The grade of sodium silicate is not stated. *See* paper by Stericker in this volume.—J. A.]

† The remarkable sedimentation apparatus of Sven Odén is also suitable. See his extensive paper in Vol. I of this series, which mentions also other apparatus.—J. A.

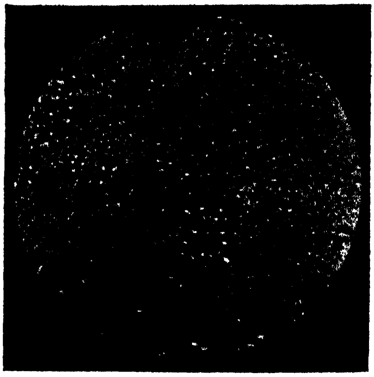
TABLE 2.

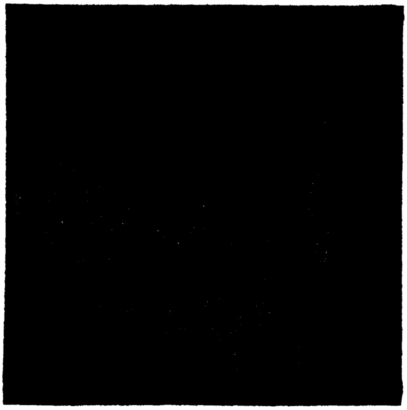
$Na_4P_2O_7$ Figured on the Basis of the Wet Paste	Dry Content of the 3 Grams Weighed (Paste + $Na_4P_2O_7$)		Calculated Content, in Grams, of the 3 Grams Weighed		$BaSO_4$ (Calculated) in the 3 Grams Weighed ($Na_4P_2O_7$ + Paste)	$BaSO_4$ (Calculated) in the Dry Weight Contained in the 3 Grams Weighed	Dry Content of the 1 Per Cent Suspension after Standing 16 Hours		Content of $BaSO_4$ in the Dry Residue	
	By Weight	Calculated	Total Dry Weight	$BaSO_4$			Calculated from the 3 Grams Weighed	Calculated in Per Cent of the Dry Content of the 3 Grams	Calculated from the 3 Grams Weighed	Calculated from the Dry Content of the 3 Grams Weighed
Per Cent	Per Cent		Grams		Per Cent		Grams	Per Cent	Grams	Per Cent
0.........	40	40	1.200	1.200	40	100	—	—	—	—
1.........	40.60	40.59	1.218	1.188	39.60	97.56	0.286	23.5	0.279	22.9
2.........	40.75	41.18	1.235	1.176	39.21	95.24	0.333	27.0	0.318	25.7
6.........	43.50	43.40	1.302	1.132	37.73	86.95	0.456	35.6	0.397	30.5
20.........	49.50	50.	1.500	1.000	33.33	66.67	1.042	69.5	0.695	46.1
50.........	60.50	60.	1.800	0.800	26.66	44.44	1.773	98.5	0.788	43.8 *

* This diminution in the $BaSO_4$ content, as compared with the preceding, is no doubt explicable by the diminution in weight of the $BaSO_4$ fraction of the $Na_4P_2O_7 + BaSO_4$ mixture.

fully settled after lapse of several days; (b) one per cent dispersions, stirred up in water, show at the end of 16 hours, from 30 to 80 per cent of the dry content afloat in the case of turbidities—suspensions had settled out completely. These arbitrary limits apply to most industrial preparations examined.

Sometimes certain cloudy dispersions show no individual particles upon being magnified 2,100 times in the dark field (reflected light)—the individual





Photomicrographs of calcium arsenate (incident light, × 2100). (A trace of the material was rubbed up in water and examined in the metallographic microscope).

Fig. 1.—This specimen was precipitated in particularly fine particles, which are individually distinctly visible.

Fig. 2.—The same specimen after being colloidally dispersed with 10 per cent sodium pyrophosphate. The individual particles are dispersed to a cloud. At this high magnification, using incident light, the diffuse scattering is so great, that focussing is difficult. The larger particles in the heterogeneous dispersion tend to slide sideways out of the field and only the finer ones which float up are seen.

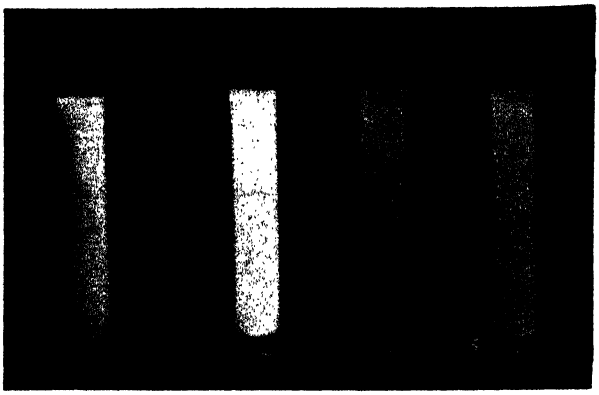
particles have vanished in the "cloudy" picture. Suspensions, on the other hand, show all individual particles under similar conditions.*

The suspension figures (*see* Table 1) of substances vary materially according to the nature of the dispersed material and the quantity of peptizer (sodium pyrophosphate). The dry samples were rubbed up in a mortar; 3 grams was weighed into a tall 300 cc. graduated cylinder, and made up to 300 cc. After shaking vigorously for one minute, the cylinder was allowed to stand quietly for 16 hours. The upper 200 cc. was then pipetted off and reduced to dryness. The weight found multiplied by $\frac{3}{2} \times \frac{100}{3}$ gave the percentage figures in the second column of Table 1.

Table 2 details the results of the five experiments listed under No. 13 in Table 1, figured on the basis of the dry content of the 3 grams used.

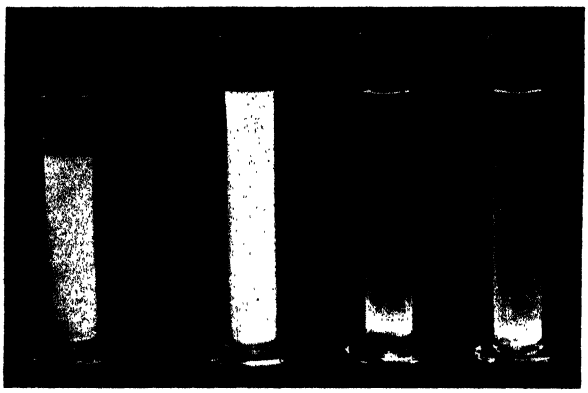
Figures 1 and 2, taken with a metallographic microscope (× 2,100, incident light), show the respective preparations at rest. Shortly after being placed on the microscope slide, the specimens, made up with the sodium pyrophosphate, exhibited the dispersion of their larger aggregates. After a few minutes

* To see individual particles, the following are essential: sufficient *dilution;* sufficiently *dark field,* with absence of very large particles (most stars can be seen only on moonless nights); powerful *illumination;* sufficient *difference in refractive index* between the particle and medium; sufficiently slow kinetic (Brownian) *motion.*—J. A.



a b c d

Fig. 3.—Relative suspensibility of 0.2 per cent dispersions; photograph taken 5 minutes after agitation.



a b c d

Fig. 4.—Same as Fig. 3, after 12 hours. Only the calcium arsenate which has been converted into a turbidity by peptisation with 10 per cent sodium pyrophosphate, has remained in suspension. (Even after 16 hours, 60 per cent was still afloat.)

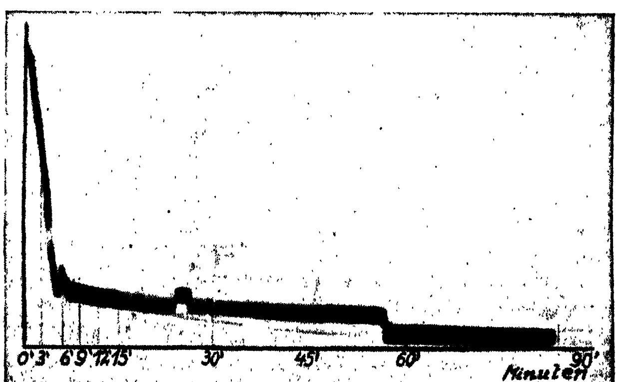


Fig. 5.—Sedimentation curve for *unpeptised* lithopone. (Reproduction of photographically registered graph, using 15 grams of material.)

the motion became less active and finally ceased. Details are given in the captions under each picture.

Figures 3 and 4 show comparatively the suspensibility of 0.2 per cent dispersions, identified as follows:

a = so-called "suspensible" commercial lead arsenate.
b = calcium arsenate, cloudy dispersion, peptized with $Na_4P_2O_7$.
c, d = two of the best American brands of calcium arsenate, for entomological use.

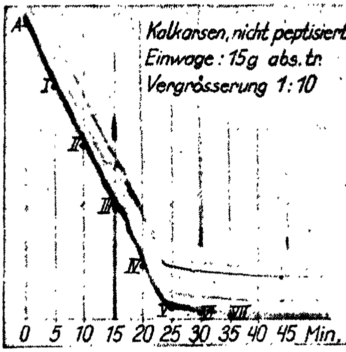


FIG. 6.—Sedimentation curve for *unpeptised* calcium arsenate. (Reproduction of photographically registered graph, using 15 grams of material.)

Figures 5, 6, 7 and 8 give the sedimentation curves, taken by Gessner's photographic attachment to the Gessner-Wiegner sedimentation apparatus,[9] of some commercial products in their original condition and after peptization with 9 per cent $Na_4P_2O_7$. The curves speak for themselves. Their significance, in terms of particle size of the settled and non-settled portions, is given numerically in Tables 3 and 4, having been calculated on the following basis:

TABLE 3.

Lithopone in its Original State			Peptized Lithopone		
Time of Fall Minutes	r (in μ) of the Particles Completely Settled Out	Per Cent	Time of Fall Hours	r (in μ) of the Particles Completely Settled Out	Per Cent
5	up to 19.12	51.9	½	up to 8.15	11.8
6	19.12 to 17.45	31.7	1	8.15 to 5.76	
over 6	less than 17.45	16.4	2	5.76 to 4.07	
			10	4.07 to 1.82	
			20	1.82 to 1.29	36.4
			30	1.29 to 1.05	12.9
			over 30	less than 1.05	38.9

The ordinate of any point on the curve gives the weight in per cent of the particles still afloat. According to Stokes' formula,

$$r = 3\cdot\sqrt{\frac{\eta v}{2g(D-d)}};\ \text{or on substituting } v \text{ by } \frac{H}{t},$$

$$r = 3\cdot\sqrt{\frac{\eta H}{2gt(D-d)}},\ \text{where}$$

r = radius of the particles in centimeters.
η = viscosity of dispersion medium (= 0.01 for water at 20° C.).
v = velocity of fall of particles in cm. sec.$^{-1}$
g = acceleration due to gravity in dynes = 981.
D = specific gravity of the disperse phase.
d = specific gravity of the dispersion (=1.0 for water).

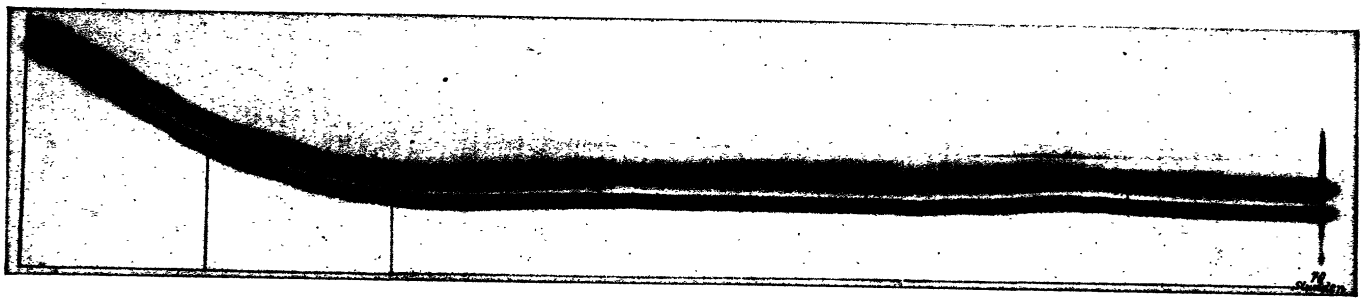


FIG. 7—Sedimentation curve for *peptised* lithopone. (Reproduction of photographically registered graph, covering 70 hours, using 15 grams of material.)

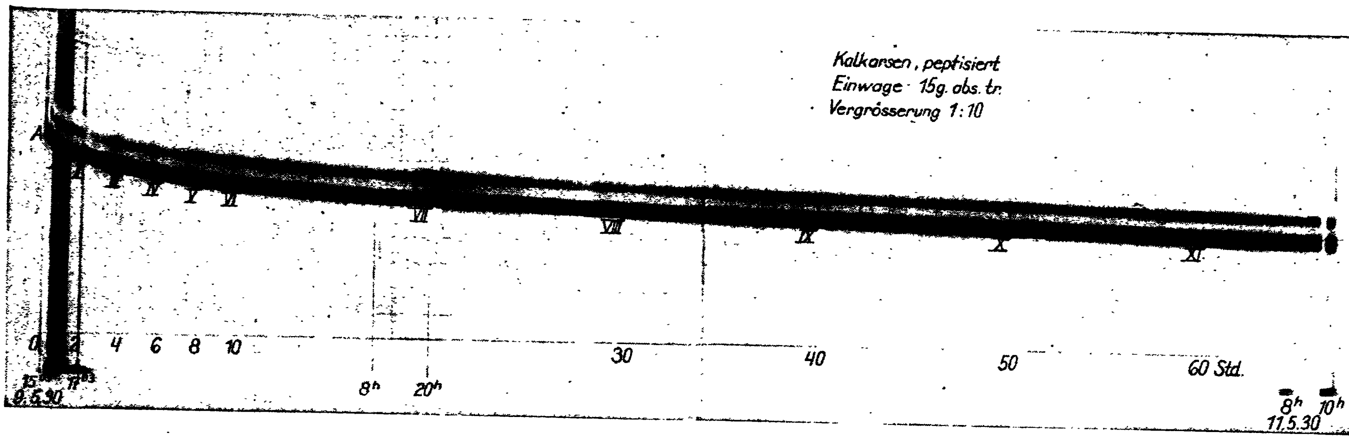


FIG. 8.—Sedimentation curve for *peptised* calcium arsenate. (Reproduction of the photographically registered graph, covering 60 hours (std) on 15 grams of material.)

This gives the diameter of any particle (r_1), falling in a given time (t_1). After the lapse of time t_1, particles of radius r_1 and over will have settled out, but finer particles will remain afloat. A tangent is drawn to the point on the

TABLE 4. *Unpeptized Calcium Arsenate: Dry Weight, 15 Grams, D = 2.857.*

Time of Settling Minutes	Height of the Ordinate on the Photogram m.m.	Amount Afloat Grams	Amount Settled Out		Amount Afloat Per Cent
			Grams	Per Cent	
5	61.5	11.96	3.04	20.3	79.7
10	46.0	8.85	6.15	40.0	60.0
15	30.0	5.84	9.16	61.0	39.0
20	14.0	2.72	12.28	82.0	18.0
25	2.6	0.51	14.49	96.7	3.3
30	1.5	0.29	14.7	98.0	2.0
35	0.5	0.10	14.9	99.4	0.6

Peptized Calcium Arsenate: Dry Weight, 15 Grams, D = 2.879.

Time of Settling Minutes	Height of the Ordinate on the Photogram m.m.	Amount Afloat Grams	Settled Out Grams	Settled Out Per Cent	Amount Afloat Per Cent
1	70.5	13.67	1.33	8.86	91.40
2	67.0	13.00	2.00	13.33	86.67
4	63.0	12.22	2.78	18.55	81.45
6	60.5	11.73	3.27	21.8	78.20
8	58.6	11.37	3.63	24.2	75.80
10	56.9	11.02	3.98	26.5	73.50
20	52.4	10.15	4.85	32.4	67.60
30	49.7	9.63	5.37	35.8	64.20
40	47.2	9.15	5.85	39.0	61.00
50	45.5	8.82	6.18	41.2	58.80
60	43.8	8.50	6.50	43.4	56.60

curve representing the time t_1; then we have from Figure 8 the following proportions *:

$100 \times AB : AO$ = total percentage weight of particles in the sample with radius $\geqq r_1$
$100 \times BC : AO$ = percentage weight of particles with radius $<r_1$, already settled out, at time t_1, and beneath the fluid level prior to beginning estimation
$100 \times CD : AO$ = total percentage weight of particles with radii between r_1 and r_2
$100 \times DE : AO$ = percentage weight of particles with radius $<r_2$ settled out within the time t_2
$100 \times AC : AO$ = percentage weight of particles of all sizes settled out in the time t_1
$100 \times AE : AO$ = percentage weight of particles of all sizes settled out in the time t_2.

Evaluation of the Calcium Arsenate Curve, with Respect to the Weight of the Particles Still Afloat.

In order to calculate the amount of the disperse phase still floating in the dispersion medium, the height (see below) is measured and inserted in the following formula: $p = \frac{H_1 - H_2}{H_2} \cdot \frac{DV}{D-1}$,

where p = amount of disperse phase still afloat; D = specific gravity of disperse phase; V = combined volume of disperse phase and dispersion medium; H_2 = height of the column of the mineral suspension; H_1 = height of the water column.

The value of p was determined on a 15-gram sample, and the percentage calculated from the formula $\frac{15 - p . 100}{15}$. Results on lithopone and calcium arsenate are given in Tables 3 and 4.

* B and D are the points where tangents to the curve at the points t_1 and t_2 cut the axis of ordinates; C and E are points where the abscissas of the points t_1 and t_2 cut the /.

These few examples of peptization to cloudy dispersions or turbidities differ from cases heretofore made and studied not only in that solid non-gels were used, but also in the nature of the peptizers applied to such solid non-gels. Contrary to usual practice in peptization, peptizers with high OH- or H-ion concentration are not used. The ionic character of the peptizers employed is relatively small.

Peptization to turbidity approximates the *hydrotropy* discovered by Neuberg, as well as the processes leading to formation of emulsions. Thus hydrotropic salts, turbidity-peptizers (dispersators), and emulsifiers are characterized by long atomic groups, which contain polar water-attracting centers. Besides, in the case of turbidities, the peptizers are polar substances, with eccentrically disposed mean force centers, which though unable to produce solubility of solid non-gels, at any rate leads them to the preliminary step—orientation.*

The earlier view of F. V. von Hahn, according to which any substance may be brought into colloidal dispersion, if only the suitable peptizer be found, is refuted by the experiments above referred to, at least in the case of solid non-gels, which give only turbidities, even with oriented substances attached. Substances suitable for this purpose are merely oriented, with polar structure, and must not be very active (that is, must not be strong electrolytes). They can not form complexes and can not, therefore, form sols from non-gels. On the other hand strong electrolytes like NaOH, HCl have no colloidizing action on solid non-gels which lack solvate films. Such electrolytes lead, rather, to molecular solution.†

To summarize: Where no solvates are present, from solid non-gels there are formed only turbidities, provided that there are used as peptizers only substances which are polar and relatively slightly active. Solvates, on the other hand, form sols, but require as peptizers very active molecules having the power to form true compounds which can fasten themselves to the particle surface. The slightly active polar substances which serve as peptizers for solid non-gels, are incapable of orienting themselves on solvates.

* Of interest in this connection are the papers of McBain and Alexander, P. P. von Weimarn, and N. Rashevsky in this volume. Within very close ranges, molecular forces increase at a much higher exponential rate than the inverse square—possibly the inverse fifth to eighth power. Once the particles are separated slightly by a preliminary absorption of dispersion medium (with or without added "agent"), subsequent and further dispersion becomes easier or may be spontaneous. Thus before redispersing rubber with colloids like clay, gum, etc., it is first swollen in a "solvent" like benzene or gasoline. Selenium oxychloride, studied by V. Lenher [*J. Am. Chem. Soc.*, 43, 29-35 (1921)] is a curious solvent, dissolving such diverse substances as rubber and gelatin, and even causing barium sulfate to swell to a jelly.—J. A.

† An interesting case is that of alumina, studied colloid-chemically by R. Zsigmondy (*Goettinger Nachrichten*) and V. Kohlschütter (e.g., Canadian patent 229,948, March 27, 1923). *See also* paper on "Fibrous Alumina" by P. Wislicenus in Vol. I of this series. Depending on the nature of the original product, alumina may be dissolved molecularly, colloidally, or remain unaffected by HCl. R. Willstätter (*see* his paper in Vol. II of this series) used special aluminas in the *elution* of enzymes. *Alucol* (Kohlschütter), made by immersing alum crystals in caustic alkali, is peptized by HCl and adsorbs acid in cases of hyperacidity.—J. A.

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[7] A. Chwala, German Patent C 43,554. (*See also* papers on Flotation by Buchanan and on Water Japan by Davey in this volume.—J. A.)

[8] *See* F. V. von Hahn's splendid book "Dispersoidanalyse" (Dresden, 1928).

[9] *See* R. Lorenz and O. Seiderer, Untersuchungen über Dispersität und Weissgehalt der Papierfüllstoffe, *Wochschr. Papierfabr.* (1927).

Suspensoids and Their Electrical Precipitation

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General Phenomena.

Suspensoids (S) consist of liquid or solid particles suspended in a more or less uniform medium (M) such as a gaseous or liquid fluid. Essentially all the form and structure of the visible world is due to the distribution of suspensoids in it. The nebulae and all structures of the heavens consist of "clouds" of particles and "points" of light such as the stars. The "points of light," the stars, when sufficiently near to us like the sun, are found to be surrounded by corona "flames" sometimes a million miles in length or covered by sun spots. In our own atmosphere we would see very little if anything were it not for suspensoids. The splendors of sunrises and sunsets and perhaps even the blue color of the sky are due to suspensoids. The reason that suspensoids determine so much of the contour, the color and the structure of the visible world is due to the condition that atoms and molecules refract and reflect only the shorter wave lengths of radiation such as X-rays. If we could see by X and γ rays our world of sight would be that of electrons, ions, atoms and molecules. As it is, the world of vision is a suspensoid world, structures consisting of aggregates of particles of solid or liquid matter, refracting and reflecting light from certain bounding "surfaces."

The birth stage of suspensoids is usually "sudden" while the length of life is frequently very long. Geological history is written by the suspensoids in the rocks, well illustrated by "sand," by the radioactive pleochroic "halos" or by the cell structures of animals and plants. Human history is written by the suspensoids of ink. Stellar history is largely the spectroscopic history of luminous "flames" surrounded by absorbent gases or gases "excited" to luminosity by "suspensoid" radiations. The "permanency" of the world is essentially the permanency of suspensoid surfaces. The nature of the "birth" of suspensoid surfaces is not well known. Many, if not all of them, are formed in a region of ionization and of electric fields. CH_4, a gas, burns with a "flame," producing some suspensoid, carbon smoke. Carbon smoke can be formed under conditions such that the suspensoid particles are small diamonds. If we could control the growth of carbon suspensoid surfaces we could produce diamonds.*

* The mongrel mixture of detritus called "dust" in the household, is commonly found precipitated on walls (e.g., where radiators or leaks in window casings or door jambs produce air currents), or on protected areas of floors (e.g., under beds or other furniture). The phenomenon is something quite apart from the quiet settling of fine particles according to Stokes' law, which causes the ordinary layer of "dust." It seems to involve an electrical precipitation and/or aggregation, whereby particles which have specific surface charges or which have become charged by adsorption of atmospheric charges (electrons, ions, or smaller particles), attach themselves to wall areas or to other particles having opposite specific or net charges.

It would be an interesting research to see to what extent (if any) dust becomes charged by metal or other radiating surfaces, by friction due to air currents, and by sunlight. That horror of efficient housewives, known in New England as "house-moss," appears to consist of a fluffy mat of adventitious fibers (cotton, wool, linen, silk) whose electrostatically active surfaces aid in holding them together and in fixing on them other kinds of dust particles. J. A.

In the process of electrical precipitation we employ phenomena that duplicate many if not all the conditions under which suspensoids are born, conditions of ionization and the presence of comparatively intense electric fields. Perhaps ultimately the greatest value that the development of the process of electrical precipitation will provide will be that of the control of the growth and the structure of suspensoid surfaces, the "separation," the "sorting," the "precipitation" and the "collection" of particular forms of solid and liquid matter.

The first stage in the technical process of electrical precipitation consists in the ionization of the medium containing the suspensoid. In practical applications this medium is usually a gas. The gas is ionized into electrons (e), negative ions (e) and positive ions (p). Neutral molecules of the fluid, Σep, are not ionized directly unless they happen to be in the vicinity of the active electrode of the electrical precipitator. The suspensoid particles may carry a charge acquired from the ions produced in the smelter or other source, but this ionized suspensoid is to be avoided, as it may be charged to a sign opposite that of the ionizing or active electrode and be precipitated upon it. Patents [1] have been issued to cover processes of removing the ionized suspensoid particles before they enter the electrical precipitator. The differently charged ions produced in the "corona" about the active electrode are "separated" into two streams of ions by the electric field (E) (say a wire in a cylindrical pipe), of the electrical precipitator, the drop of electrical potential, producing corona (Vc), the voltage across the electrical precipitator (V) and the voltage causing electrical precipitation being Vp. As the active electrode is usually negatively charged in practice, this condition will be assumed in the equations.

$$Vc \text{ and } (\Sigma ep) \equiv i(\Sigma ep)^- \longrightarrow \quad + i(\Sigma cp)^+ \longleftarrow \quad + h_1 \tag{1}$$

$$Vc \text{ and } i(\Sigma ep)^+ \longleftarrow \quad + \mathrm{V}p \text{ and } i(\Sigma cp)^- \longrightarrow \quad + \Sigma SM + h_2 \equiv I \tag{2}$$

$$Vp \text{ and } [i\Sigma ep^- \longrightarrow \quad \Sigma SM] \equiv Vp + i(\Sigma ep\Sigma S)^- \longrightarrow \quad + M. \tag{3}$$

Equation (1) represents the ionization resulting from the breakdown of the dielectric and the separation of the two kinds of ions by the electric field. The ionization and the chemistry of the corona of (1) and (2) will be treated briefly in following sections.

Let us suppose the negative ions are electrons. For a coulomb per sec. of current 8×10^{18} electrons will pass. It has been estimated that as much as 18 tons of suspensoid could be precipitated by 3 kilowatts of energy. Assuming that $Vc + Vp = 40{,}000$ volts this would cost about 3 cents at the rate of 1 cent per kilowatt hour or about $7,000,000 per lb. of electrons produced, assuming that the current is carried entirely by electrons. If we suppose that the corona is produced and the current all carried by a specific kind of ion, we have at 1 cent per kilowatt of energy:

Table I.

Material Carrying the Current	Cost about	Size, Diameter about
1 lb. electrons	$7,000,000.00	10^{-13} cm.
1 lb. H_2 ions	2,000.00	$2(10)^{-9}$ cm.
1 lb. H_2SO_4 ions	20.00	$(10)^{-8}$ cm.
1 lb. dust $(10)^{-7}$ cm. diameter	.02	$(10)^{-7}$ cm.
1 lb. dust $(10)^{-6}$ cm. diameter	.00002	$(10)^{-6}$ cm.
or about 2¢ per ton.		

The above table is only approximate and indicates the minimum cost of electrical precipitation, when each dust particle is charged and all the current

is carried by the dust particles. From equations (2) and (3) it follows that the maximum current carried by the suspensoid ΣS is only one-half the total current. In many cases a large part of the current or even all of the current may take the form of a capacity current, such as the surging of space charges. The disappearance of the corona at high frequencies is due to the surging of the space charges becoming so rapid that its period approaches the time period of the molecules and ions over their mean free path. (h_1) and (h_2) are quantities indicating the change of electrical energy into heat energy and are registered partially as "corona pressure" and increase of temperature of the parts involved. $i(\Sigma ep)^{-}\rightarrow$, $i(\Sigma ep)^{+}\leftarrow$ and $i(\Sigma ep\Sigma S)^{-}\rightarrow$ represent "directed streams" of high temperature, various types of electrical or "brush" discharges and the "electric wind." In electrical precipitation a very few of the ions, $i(\Sigma ep)^{-}\rightarrow$, combine with the suspensoid, ΣS, so that but a small percentage of the ions are useful in charging the suspensoid. Notwithstanding this fact that only a small percentage of the ions combine with the suspensoids, electrical precipitators rarely use more than from 1 to 60 milliamperes of current.

In metals the electrons are "free" to move on the impression of a very weak electric field, so that "electrical precipitation" here consists in the precipitation of electrons. Power transmission is electron precipitation made possible by the small mass of the electrons. In electrolytes the "ions" are formed and move under potential gradients of a few volts and as ionization is frequently spontaneous the cost of the separation of ions is thousands of times less than it is in the case of gaseous ionization in coronas. "Corona chemistry" may possess a great theoretical value but little commercial usefulness. In dielectric liquids corona is formed with difficulty.[2] Crago and Hodnette obtain corona in oil when V is 55,000 volts r.m.s.

Commercial electrical precipitation of suspensoids is almost wholly limited to the cleaning of gases. The suspensoid may consist of any dust, cloud, mist, fume, smoke, odor, bacteria or "opacity" suspended in any gas. The electrical precipitator consists of wires, chains, small rods or other like-shaped electrodes placed symmetrically within plates, cylinders, pipes or like-shaped electrodes, the two systems being connected to a source of electrical potential which may vary from 2,000 to 250,000 volts, though usually ranging from 35,000 to 80,000 volts. The suspensoid usually moves in the direction of the electrodes or normal to them. The direction of the electric field is normal to the electrodes and the direction of the precipitation of the suspensoid is the resultant motion due to the velocity of the gases through the precipitator (V_{MS}) and the velocity due to the electric field (V_E). If V_{SM} is too great the suspensoid is not removed or at least not completely removed from the gas. For fairly complete cleaning and for electrodes say ten feet in length V_{SM} should not greatly exceed ten feet per second.[3] The suspensoid gases only require from one to three seconds to pass through the ordinary electrical precipitator.

The electrical equipment includes proper induction coils, transformers, switchboards, rectifiers, insulators, generators, cut-outs and measuring instruments. High voltage transformers giving up to 80,000 volts at from 30 to 60 cycles and Lemp rectifiers commonly serve as the source of electrical potential. In thunderstorms we have precipitating voltages as high as 100,000,000 to 300,000,000 volts and in electrical engineering 1,000,000-volt transformers are available but these higher voltages are not at present suitable to commercial electrical precipitation. The important condition is an intense electrical potential gradient (E) rather than very high values of V.

The process of electrical precipitation can be combined with the use of

bags, screens, settling, centrifuging, semi-permeable surfaces, magnetic action, differential chemical or condensation action, spraying, sand or other blasting, radiation pressure, acoustic high frequency waves, the inductive and aggregating effects, and no doubt the future will witness many unique and effective combinations of these methods. In the meantime electrical precipitation engineers are confronted with many problems such as the maintenance of insulation especially at high temperatures, the distribution of the gases through the various parts of the treater, the cleaning of the electrodes, the operation of treaters when the gas temperature and velocity vary greatly, the cumbersomeness of the treaters, etc.

Applications of Electrical Precipitation Processes.

The first commercial electrical precipitator was set up in England by Lodge and Walker in about 1881. As they depended upon the electrostatic Wimshurst machine for their supply of high voltage current, their precipitator could be made to collect only a very small quantity of fume. Their method of using a barbed wire electrode in a chimney, that is a wire axially placed in a conducting cylinder as the collecting electrode and passing the suspensoid along the electrodes remains today as the standard method in practice and in theory. The current per unit length of such a precipitator is the precipitating current (I).

F. G. Cottrell [4] succeeded in precipitating sulfuric acid mist, copper smelter fumes and cement dust in a commercial way because he used transformers and Lemp rectifiers [5] to produce his precipitating high voltage current (I). In the early work, from 1905 to 1910, the transformers available did not give sufficiently high voltages to produce proper corona ionization $[i(\Sigma ep)]$ so the "pubescent" electrode was used. This type of electrode has been discontinued.

For a description of the apparatus one should consult the technical metallurgical and electrical journals [6] and the patent literature.[7]

The application of commercial electrical precipitation was hastened by the condition that many kinds of acid fumes, smelter and cement dust constitute a nuisance in suburban and agricultural communities.[4] The city smoke problem inspired the Mellons of Pittsburgh to start the Mellon Institute, one of whose first problems consisted in the problem of abating suspensoid nuisances.[8] The more recent development of the electrical precipitation processes has been in the industries themselves, including Europe as well as America. Electrical precipitation has been employed to remove dust from gases [9] such as is made in the briquet industry in Germany, in coke ovens, in illuminating gas plants, in sulfur burners, in gas producers and in oil shale distillation; to remove tarry matter from water and illuminating gas; [10] to remove dust from the gases of pyrite burners; [11] to remove H_2SO_4 and other acid mists from gases; [12] to clean blast furnace gas, to remove dust in the grinding industries, to remove cement and magnesite in these industries, to remove dust in the cellulose industry; [12] to collect volatilized phosphoric acid; [13] to produce phosphoric acid in the pyrolytic process; [14] to clean producer gas; [15] to make a quantitative determination of the size, shape, weight and density of suspensoid matter by precipitating it under known conditions and studying the precipitate; [16] to deodorize a gas by the removal of the very fine particles that serve as the source; [17] to remove bacteria (such as may cause influenza), dust, fumes (such as diphenylchlorarsine) of a poisonous nature from the air that one breathes by using a small special type of electrical precipitator in a fume mask; [18] to

aid the process of pollenization by ionizing pollen grains and making plants a part of the electrode system of an electrical precipitator; to separate suspensoids of different volatilities by their fractional precipitation at different temperatures;[19] to remove lachrymator or tear-producing fumes;[18] to produce metallic surfaces by metallic sputtering; to separate the isotopes of the chemical elements;[20] to clean hot gases before they are burned in stoves or used for drying purposes;[21] to clean the gases of combustion that are to be used for other purposes; to clean the air of buildings so that it can be used a number of times without reheating, thus conserving its heat energy;[22] to recover the black ash and clean the hot waste gases for drying purposes in the pulp and paper industry;[23] to remove nuisance fumes, dust or smoke;[24] to debloom mineral oils of their fluorescent material;[25] to collect potash, precious metal dust, lead smelter fumes, zinc oxide, fertilizer dust, diamond dust, carbide, alumina and gases that can be made to be absorbed or combined with suspensoid material;[26] to condense smoke on meat or on salts to be used to cure meat; to condense ionized material in the lungs for germicidal purposes; to produce rain under especially suitable conditions by pouring electrified sand upon air highly saturated with water vapor from an airplane;[27] to clean the air over large cities in order to permit the ultra-violet light of the sun to reach the ground line;[28] to indicate and record the density of fumes and smoke by means of an electrical suspensoid recorder;[29] to separate water from oil;[30] to analyze certain gases by the nature of the corona chemical effects; to collect volatilizable products in qualitative and quantitative chemical analysis; to serve as an electrical voltmeter through the resultant increase of pressure due to corona ionization; to serve to indicate extremely small intervals of time in terms of Lichtenberg figures, intervals as small as a microsecond, by the klydonograph;[31] to electrify the insectide fumes positively for spraying the negatively charged orchard trees and cotton plants; to enable us to understand the nature of "double layers"; to effect the separation of pulverized materials as in the Huff electrostatic process;[32] to apply the electrical precipitation methods to conditions where ionization already exists as in dialysis, electrolysis, electrodialysis, osmosis, electro-osmosis and electro-ultrafiltration,[33] and perhaps to collect ultra-fine material as the so-called bacteriophage (estimated diameter $2(10)^{-6}$ cms.).

When one fully recognizes the rôle that ionization and the electric field have played in the development of our newer physics, chemistry and astronomy, when one recognizes that there are numerous 1,000,000-volt laboratories[34] and that the subject of high voltage science and engineering is in its infancy, one can hardly overemphasize the number and the extent of the various fields of application of the processes involved in electrical precipitation. The use of a klydonograph as a "direction finder," using intervals of microseconds or less, in much the way that our own ears differentiate time intervals from 10 to 5 microseconds in determining sound directions may alone be of transcendant value in warfare.

At the same time that higher and higher voltages are being made available, the world of the infinitesimal is becoming better known. Electrical precipitation depends upon an electrical potential gradient and the most intense potential gradients are located at the "surfaces"[35] of electrons, atoms, molecules, ions, and solid and liquid particles and bodies. Phenomena of filtration, screening, absorption, adsorption, catalysis and even chemical reactions may eventually be expressed, like electrical precipitation, in electrical equations. Eventually the electrical processes will be found to play a major rôle in biology and even in psychology. "Double layers" and especially the collection of sus-

pensoids such as zinc oxide in bags illustrate how electrical conditions are involved. As an example Harkins claims that the surface layer of an aqueous salt solution contains only H_2O molecules, the solute is "precipitated" from the surface layer, leaving only pure water. The theory of "electrical precipitation" by electron, atom and molecular fields remains as a "new country" for research investigation.

Ionization and the Life Histories of Ions.

In all dielectrics, such as gases, there are always a few ions forming and recombining. The rate of formation of this so-called "spontaneous" ionization in air is only a few ions per cu. cm. of volume per sec. Some of this ionization is due to radioactive material and some to the penetrating radiation, part of which is claimed to be due to a very hard ultra-γ radiation from interstellar space. Whenever there is an electric field gradient of about 30,000 volts per cm., such as exists near the active electrode of an electrical precipitator, the few ions already existing there are given such high velocities (high temperatures in the direction of the radius of the precipitator pipes) that they generate other ions by collision, $i(\Sigma ep)$, thus producing the corona. The process of ionization is being put upon a quantitative foundation in the case of gases at low pressure and eventually these methods will be applied at ordinary pressures. For electrons falling through 100 volts at 1,000 bars at 20° C., the number of elastic collisions Pe, inelastic collisions Pk, ionizing collisions Pi (inelastic) and resonance excitating collisions Pr (inelastic) have been given by Langmuir and Jones [36] as follows:

Table II.

Gas	Pe	Pk	Pr	Pi	Vr*
Hg	19	33	10	23	6.7
A	10	14	1.3	12	13
N_2	7.8	12.2	3.6	8	13
H_2	4.8	7.1	2.8	4	12

* Resonance potential in volts.

In an electrical precipitator the ions may vary in size from the electron whose estimated radius is 10^{-13} cms. up through small molecules of 10^{-8} cms. radius (0.01 mμ), large molecular sizes (the egg albumen molecule [37] is estimated to be $52.8(10)^{-8}$ cms. long), aggregates or dispersoids into particles that are visible (10 mμ) in the ultramicroscope. In their study of "smokes" produced by the sudden cooling of a saturated vapor, Whytlaw-Gray, Speakman and Campbell [38] find an unstable initial period when the particles increase rapidly in size and a stable period after the lapse of several hours. Young [39] has measured the mobilities of ions produced in coronas at atmospheric pressure and finds that there are groups of ions. For O_2, N_2 and CO_2 the mobilities range between 0.7 to 10^{-5} with nearly all mobilities less than 10^{-2} cms. per sec. per volt per cm. Positive and negative ions were about equal in number. Erikson finds that acetylene in air, air, CO_2, H_2 and Ar all have a negative ion of the same mobility. With the exception of acetylene, the initial stage of the positive ion only lasts a fraction of a second.

In the case of suspensoids the nature of the life histories of the particles is much more complicated. Some of the properties of these large ions have been given as follows, according to Walther Deutsch: [40]

Radius of particle in cms.........	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}*
Size of charge (times e)	4640	376	28	2	1	1
Migration velocity, 1 c.g.s. cm./sec.	0.69	0.56	0.42	0.35	1.5	450

* Molecular size.

Delasalle [11] obtains a mobility (K) of $0.4(10)^{-2}$ at 230° C. and $0.57(10)^{-2}$ at 310° C. for dust from pyrite burners ($FeSO_4$, 24; FeO, etc., 25; $PbSO_4$, 39; As_2O_3, 8 per cent). Pescal [12] finds a mobility (K) for H_2SO_4 mist ions to be $0.15(10)^{-2}$ at 55° C. and $0.24(10)^{-2}$ at 24° C. The radii varied from $0.8(10)^{-4}$ to $5.5(10)^{-4}$ cms. and the number of particles varied from 300,000,000 to 1,000,000,000 per cu. cm.

The life histories of suspensoids have been studied but slightly and require a much fuller knowledge of the nature of the force fields about the suspensoid particles. The subject is of the greatest importance in connection with the formation of clouds, rain, hail, snow, the production of smoke screens and "poison gas" clouds in warfare and in spraying insectides.*

The law of force (Fi) between a molecule and an ion is invariably assumed to vary inversely as the fifth power of the distance between the molecule and the ion (r).

$$Fi = \frac{(D-1)e^2}{2\pi N r^5} \tag{4}$$

D is the dielectric constant of the gas, N is the number of molecules per cu. cm. of volume, M is the mass of the molecule, m the mass of the ion, ρ_0 the density of the gas under n.t.p., and ρ the density under the given condition. Langevin [41] derives

$$K = \frac{1.7(10)^{-3}\rho_0 \sqrt{\frac{M+m}{m}}}{\rho\sqrt{(D-1)\rho_0}} \text{ cm./sec./volt/cm.} \tag{5}$$

But the nature of the ions is not well understood. Franck [42] and Weitner found that old ThD ions had the same mobility as air ions (1.4 cm./sec.). Erikson [43] finds new ThD ions to have $K = 4.35$ cm./sec., perhaps due to their double charge.

Gas	Air	H_2	HCl	Ether	CO_2	CH_3I
K	1.4	6.02	0.65	0.19	1.4	1.4

In pure N_2, He and H_2, electrons remain comparatively "free" whereas in HCl and Cl_2 they quickly attach themselves. Erikson finds K for new ions in all gases to be the same. In 0.001 to 0.03 secs. K for the positive ion becomes normal. He assumes old + ions to be bimolecular. In gas mixtures there is evidence of clustering.

The current density at any point in an electrical precipitator in terms of the density of the ionic space charge ρ is

$$i = \rho K E, \quad I = 2\pi\rho r_0 K E = -\frac{2\pi\rho r_0 K V}{r_0 \log R/r_0} \tag{6}$$

Here the relation between the electric field and V for a corona of radius r_0 is assumed to be unaffected by space charges, r_0 being the radius of a "metal" or "conducting" cylinder. Poisson's equation gives ρ and finally C_1 for conditions when corona starts

* *See also* paper by W. A. Gibbs in Vol. I of this series. J. A.

$$-4\pi\rho = \frac{1}{r}\frac{d}{dr}\left(r\frac{d\varphi}{dr}\right),\ \frac{d\varphi}{dr} = -E_o,\ r\frac{d\varphi}{dr} = -2\pi r^2 + C_1 \tag{7}$$

integrating between the limits $r = a$ and $r = R$ and neglecting a^2 compared to R^2,

$$V = -4\rho(R^2 - r_c^2) + V_o = -\pi R^2\rho + V_o;\quad I = \frac{2KV(V - V_o)}{R^2 \log (R/r_c)} \tag{8}$$

Fazel and Parsons find currents as high as $i = 25(10)^{-6}$ amp. per cm. and $\rho = 2.2$ e.s. units.

"Slow Motion" Electrical Precipitation.

The electrical precipitation of smoke and fumes has always been of interest to the observer, both lay and scientific. Movies have been made of the process. Tolman and Karrer [44] have photographed the streams of turpentine droplets, water jets, Al and Zn particles, as these are precipitated by the corona discharge. Perhaps the most valuable form of electrical and magnetic precipitator is the mass spectrograph of J. J. Thomson and Aston used to separate the isotopes of the chemical atoms.

A very interesting form of electrical precipitator is that used by Millikan [45] to study the motion of charged particles such as oil drops. Individual charged particles were held "precipitated" in space in front of a microscope by balancing the force of gravity by the force of the electric field or by allowing the charged particle to "move slowly" through the field of the microscope. The purpose of these experiments was to determine the law of motion of precipitated charged particles in an electric field. Millikan could study the "slow motion" of the precipitation of a single droplet much more accurately than Thomson and Wilson could study the similar "slow motion" of the precipitation of a cloud.[46]

Millikan and his co-laborers have studied the "slow motion" precipitation of many kinds of particles with varying charges and in different gases. For instance, one drop of radius 0.000658 cms. was watched 4 hrs. during which time its charge varied from 126 e to 150 e. The resistance of fall or the "resistance to precipitation" which a particle meets, F_p, is given by Stokes' law modified by Millikan. Let a be the radius of the drop, v its velocity, λ the mean free path of the molecules of the gas, η the coefficient of viscosity and A, B and c constants. (See Millikan's paper in Vol. I, this series.)

$$F_p = 6\pi\eta av\,[1 + (A + B\epsilon^{-ca/\lambda}/a]^{-1}, \tag{9}$$

where Millikan finds $A = 0.864$, $B = 0.29$, $c = 1.25$. It will be noted that the force required to precipitate a suspensoid depends upon the time of precipitation, that is, upon the velocity of precipitation. The slower the process the less work required. Settling by gravity is one of the most efficient methods of cleaning gases from the point of view of energy consumption. The energy actually used in electrical precipitation is the energy used to charge the suspensoid matter, $i(\Sigma ep)$, and $F_p x$ where x is the distance the suspensoid is removed. Integrated over the volume of the suspensoid and the distance of precipitation, the radius of the pipe in a cylindrical precipitator (R), one has the total energy used (W), du, dv, dw being an element of volume.

$$W = \iiiint i(\Sigma ep)\, dS\, du\, dv\, dw + \iiiint\int_{x=0}^{x=R} F_p x\, dS\, dx\, du\, dv\, dw \tag{10}$$

The classical problem of "slow motion" electrical precipitation is to have the apparatus automatically keep the suspensoid particle in a set position by controlling the electric field, the variation of the field with time being recorded graphically.

Corona Chemistry.

The ionization about the active electrode in an electrical precipitator is a region where electrical chemical reactions are taking place with violent unidirectional temperatures that in the limit approaches the maximum. In radioactivity, in gases at low pressures or in gases subjected to very intense electric fields similar conditions hold. The maximum temperature is reached when electrons and protons possess the velocity of light.

Among the ions of corona chemistry are O_2^+ (13 volts); O_1^+ (20 volts); "active" hydrogen;[47] H_2^+; H^+; H_3^+;[48] A^+; A^{++}; K electrons from oxygen; K electrons from nitrogen; L_1 electrons from argon; very rare negative ions in CO (due to the electrons remaining free);[49] N_1^+, N_2^+, N_1^{++}, N_2^-;[48] electrons in H_2 and He at 76 cms.;[49] CO^+, etc.

If V is the potential through which a charged particle moves and Q is the charge, the energy of the corona loss W is VQ. There may be some recombination of the ions so that Q will in general be greater than the current of charges actually carried to the electrodes. If Wc is the energy absorbed by chemical reactions, Wr in radiation, Wh in heat energy,

$$W = Wc + Wr + Wh = VQ. \tag{11}$$

The ultimate way of describing the corona will be to express the life history of each ion and integrating this for the whole corona region. The basic experiments will then consist in selecting coronas where certain uniform conditions hold for the ions and their life histories. Needless to say neither the electrical nor the electrical precipitation engineers have reached this ideal. Using cylindrical coördinates, r, θ, z where r is along the radius of the precipitator, θ is the angle in a cross section of the active and passive electrodes and z is the distance along the axis of the precipitator, then the descriptive conditions are:

$$\begin{array}{lll} r & \theta & z \\ Er & E\theta & Ez \\ Hr & H\theta & Hz \\ Vr & V\theta & Vz \text{ etc.} \end{array} \tag{12}$$

In general the electric field is along r so that $E_\theta = E_z = 0$. The magnetic effects are of a second order so that we assume $H_r = H_\theta = H_z = 0$. In the Lodge-Cottrell precipitator the gas velocity is along the axis so that $V_r = V_\theta = 0$ and in the Rathbun screen type of passive electrode $V_\theta = V_z = 0$.

For a study of corona chemistry the most important feature of the phenomena is, that after the ion has fallen through a certain voltage V_i which may range about the values of from 10 to 50 volts, ionization by collision, the formation of new ions from gas molecules and a whole series of electrical chemical reactions take place. Let $r = r_a$ at the active electrode, $r = r_R$ at the passive electrode and $r = r_c$ where the ion is formed. The tracks and the life histories[50] of the ions whose period is T_t are approximately rz parabolas, z being the direction of the axis of the electrical precipitator. Roughly

$$r_c = r_a + b\,V; \quad V = V_o \text{ when } r_c = r_a, \quad r_c = r_a + b\,(V - V_o). \tag{13}$$

The exact conditions, especially when an electrical precipitator is operating near the arcing voltage, require much more research study before they can be

expressed accurately, one reason being the irregular nature of the corona itself, it often taking a brush form.

The most valuable method of studying the ultimate nature of atoms and molecules has been the use of the electric and the magnetic fields to produce a separation and a precipitation of those ultimate entities. The "mass" spectrograph of Thomson and Aston for the separation and the precipitation of isotopes is an example of the use of this method. If the nature of valency is electromagnetic, as it appears to be, the method of electromagnetic separation and precipitation will provide an important method for the elucidation of the phenomenon. By holding ions in a field of view of an X-ray camera one may be able eventually to photograph individual chemical reactions and the tracks of ions, atoms and molecules on collision. At present the study of the collisions of slow-motion electrical precipitation should throw light on the forces involved during the collision of small suspensoid particles. It is not too much to hope for a "slow-motion" electrical precipitator that will automatically keep the suspensoid particle in a certain position by adjusting the electric field. Such an apparatus, recording certain properties such as the mass of the suspensoid particle, would be of great value in the study of germs.

Pulling Electrons out of Metallic Electrodes and Cathode Sputtering.

In ordinary commercial electrical precipitators electrons are not pulled out of the negative electrode, but if the electric field gradient (E_a) at the surface of the metal is great enough or if the temperature of the metal is high enough electrons are pulled out of metallic surfaces (in sparks, arcs and in vacua). Schottky [51] found for a wire of radius a, E_a varied from 100,000 to 500,000 volts per cm. Heated and cooled the values ranged from 400,000 to 700,000. Heating to 2,700° K., $E_a = 4,300,000$ volts per cm.

Millikan and Eyring [52] using a tungsten wire $a = 0.00123$ cm. in a cylinder of radius $R = 1.625$ cm. with a potential difference between these of V, $E_a = 228\ V$, $E_a = 400,000$ volts per cm. Increasing to $E_a = 1,130,000$, the number of electrons pulled out was increased 10,000,000 times. The number of electrons pulled out was independent of the temperature between 300° K. and 1,000° K. When the wire reddens at 1,100° K., E_a falls.

Metallic particles are also torn off the cathode and precipitated on the anode. This method may be used to make metallic mirrors.[53]

Our Atmosphere as an Electrical Precipitator.

In some respects our atmosphere is a kind of electrical precipitator. The Kennelly-Heaviside layer at a height of about 100 miles somewhat resembles the ionized region about the active electrode. If the penetrating and other short wave-length radiations are of cosmic origin these may act as the source of ionization. In the Kennelly-Heaviside layer it is estimated that there are 100,000 electrons per cu. cm. and this cloud of electrons is assumed to reflect and refract radio waves back to the earth. Near the ground the potential gradient is usually about 150 volts per meter, rising to thousands of volts per meter of elevation in a thunderstorm. In a thunderstorm we are often moving about in electric fields that are nearly as intense as those about the passive electrode of an electrical precipitator. The source of the air to earth current is unknown. Even the process of the electrification of rain drops is not known, the Elster and Geitel theory being unable to explain the origin of the charges.[54]

In the stellar atmospheres, such as the corona of the sun, we have intense electric and magnetic fields and consequent ionization. Magnetic fields of sunspots reach intensities of from 5,000 to 10,000 gauss. Stellar atmospheres therefore resemble in many ways electrical precipitators at very high temperatures.[55]

The discovery by Wilson that nuclei, either ions or very small suspensoid particles, serve as centers about which supersaturated vapors condense, has been supposed to play a very important rôle in the formation of rain and snow and the formation of suspensoid particles in various combustion and smelter operations. This condensation formation probably does not come into very prominent action in electrical precipitators because the temperature changes are comparatively small.

In G. C. Simpson's new theory, the view is held that the atmosphere is divided into strata of horizontal shells that are thermally independent. These shells are the equivalent of restraints compelling the winds to be horizontal, thunderstorms and rain squalls in the doldrums being the most noted exceptions. Clouds appear at surfaces of these thermal layers. This new theory of the stratification of the air simplifies the problem of the artificial production of rain. Bancroft and Warren [56] have claimed that they have produced rain by scattering sand upon a cloud from an airplane, the sand being charged oppositely to the cloud. The claim is made that cumulus cloud has been destroyed in this way and lightning prevented by sanding the top of a thunderstorm cloud.

If artificial rain ever becomes possible it will be so because we are thoroughly acquainted with the formation of rain drops and are able to direct a condition that is unstable from a precipitation point of view, i.e. a condition of air and water vapor that requires but little energy to change it into a suspensoid. Perhaps the cleaning of the air to permit of the passage of sunlight into cities will be easier because under these conditions the air is usually stagnant. Perhaps several Eiffel towers over London could be made to serve as the mechanical support of such a system. The solution of problems of this sort will most likely be much slower than we anticipate.

The distribution of dust and its precipitation is the basis of a theory for explaining changes of climate such as the ice ages. Dust in the outer regions of the sun constitutes one of the elements in this problem. For several years after such volcanic eruptions as Krakatoa in 1883; Mont Pelé in 1902 and Katamai in 1912, volcanic dust remained in the upper air strata for two or three years. From the size of Bishop's rings about the sun [57] it is estimated that the diameter of the dust particles was 1.85 μ. Humphreys [58] * calculates that it would require several years for this dust to fall to the ground. If it were not for the "conditioning" of the air with moisture and the process of Aitken-Wilsonian condensation the atmosphere would probably be "dusty" all the time. It has been suggested that the appearance of some planets like Mars is due to a dusty atmosphere. In the case of the sun corona streamers may extend out a million miles or more from the sun.

The Electric Centrifuge.

Centrifuging is well adapted for removing the larger suspensoid particles either from gases or liquids. There are some five hundred applications of the mechanical centrifuge. By combining the electrical precipitator with the whirling motion of gases McGee and Nesbit [59] aimed to remove the finest as

* *See* paper on "Colloids in Meteorology" by Humphreys in Vol. I of this series. J. A.

well as the coarsest particles. In France Marx and Rozières[60] clean liquids by combining the use of a mechanical centrifuge and an electrical field of 40,000 volts in a bowl of 0.6 m. with a speed of 2,700 r.p.m. It has been claimed that gases traveling with a velocity of 40 ft. per sec. have been cleaned by the electrical centrifuge. By using methods of this kind it should be possible to concentrate the smallest particles such as "anti-bodies," "bacteriophage," vitamines, hormones and the supposed "germs" of cancer, if these are larger than the molecules of ordinary liquids and gases. The mathematical possibilities of these various methods of matter separation will be found in the literature treating the problem of the separation of isotopes.*

The application of an electrical centrifuge also admits of the use of slightly higher voltages because the gases are in rapid motion. It would be natural to employ the condensed type of electrical field with the centrifuge principle, using, if necessary, sand or other material for "washing" the electrodes. There remains a whole new field of research on the investigation of the precipitating powers of the corona or the electric wind in the more intense forms as they exist in condensed electric fields. The problem of space charges, whether in the precipitated suspensoid matter or in the gas, becomes more and more important as condensed electric fields are employed.

Porous Electrode Precipitators.

In the early electrical precipitation work of Cottrell and others the suspensoid gas mixture could either be passed along the direction of the electrodes or the electrodes, such as wires and plates, could be positioned in a staggered manner with open spaces permitting the suspensoid gases to flow perpendicularly to the direction of the electrodes, i.e., in the direction of the electric field itself. Rathbun[61] has improved this scheme by using metallic screens for the passive electrode.

In a few conditions alternating current precipitation has been found to take place but as a rule unidirectional currents have been employed. In the early development no means were employed to increase the electric field intensity between the active and passive electrodes though various devices were employed to prevent any condition of continued spark or arc flash over between the precipitator electrodes. Hahn[62] claims that the wire-screen type of electrode is the more efficient. A Siemens precipitator was employed to remove coke dust from generator gases, fumes from pyrites burner gases, smoke from lignite burners and dust from blast furnace gases.

The Condensed Electric Field Precipitator.

In the very early development of the process of electrical precipitation the induction coil was the most available source of high voltage current and it was natural to use it as the source of voltage in the precipitator. Induction coil high voltage current will cause some precipitation but the method is not efficient. The same limitation is found to hold for the alternating current transformer though for small pipes of say 3 in. diameter precipitation is fair.[63] It seems that the explanation of the precipitation in small-sized precipitators can be based upon the view that the charged suspensoid particles are precipitated in a period that is less than the half cycle period of the alternating electric field. In case an induction coil is used, as the oscillations are

* *See* paper by The Svedberg in Vol. I of this series; also his classic work on the proteins published mainly in *J. Am. Chem. Soc.* J. A.

much shorter than in the case of the a.c. transformer, it is to be expected that the length of track of precipitation would be further reduced. At the same time the writer found that [64] the use of a dielectric or a high resistance material between the active and passive electrodes permitted these electrodes to be brought closer to each other and that the "corona" was thus intensified and precipitation improved.

The "condensed electric" field method of electrical precipitation is useful in small electrical precipitators such as those used to record fumes and smoke, fume masks, precipitators employing comparatively inexpensive electrical equipment, electrical precipitators used to take samples of the suspensoid material in gases, precipitators such as those employed to precipitate material in the lungs, where electrical discharges are to be prevented and even in large sized installations where flash over [65] between the electrodes is to be prevented. Any medium that offers high resistance to the precipitation current is suited to this purpose. The future for the condensed electric field precipitator is very promising from a number of different points of view. Precipitators of this kind costing as little as ten dollars can be purchased. The dielectric properties of the suspensoid are extremely important factors in the "condensed electric" field precipitator.

Many smokes such as soft coal smoke, acid fumes and copper plant roaster smoke from mechanical reverberatory furnaces, are conducting. Copper converter smoke arising from copper matte converting and copper blast furnace smoke from smelters using charges low in lead, zinc and arsenic are fairly good conductors. Copper and lead blast-furnace smoke containing considerable lead, zinc and arsenic, copper reverberatory furnace smoke, lead plant roaster smoke, converter smoke from a leady matte and zinc oxide are examples of suspensoids of high resistance.

Some Practical and Theoretical Aspects of Electrical Precipitation.

(a) In the general application of the electrical precipitation process the suspensoid gases are cleaned of from 90 per cent or more of their suspensoid matter on traveling ten feet or so at a velocity of from five to ten or more feet per second. Pipes from five to ten or more inches in diameter or their equivalent in plates or other types of electrodes are employed. To calculate the size of a precipitator and its cost will depend largely upon the volume (V) of suspensoid gases to be cleaned. The location of an electrical precipitator is frequently an important factor as to its cost. Anderson [66] has given the following formula for the size (x) of an electrical precipitator, where b is a function of a unit size precipitator, c the value of the solids carried and d is a function of the "specific precipitation ratio of the fume."

$$x = \frac{V[\log b - \log (c \log d)]}{\log d} \tag{14}$$

(b) The temperature of the suspensoid gases is an important factor because at higher temperatures the character of the corona may change. Changes of temperature are accompanied by volume changes of the suspensoid gases and changes in the flash over voltage.

(c) In applying the electrical precipitation process to new or not-well-known conditions it is advisable to experiment with a small or "unit" size precipitator under typical conditions.[67]

(d) In electrical precipitation the actual precipitation process as given by equation 7 is mechanical and hence is independent of chemical conditions, the chemical nature of the suspensoid and the chemical nature of the gases.

(e) It is the electrical discharge, the ionization of the gases, the charging and the discharging of the suspensoid particles that depends upon the electrical and the chemical nature of the suspensoid particles and gases. The suspensoid gases pass through an electrical precipitator in two or three seconds while most of the suspensoid is precipitated during the first second.

(f) The theory and application of electrical precipitation start with the corona discharge as the first necessary condition for commercial work. The corona has been the subject of very extensive research work by the electrical engineers. The main objective of the electrical engineer is to prevent the power loss that results from corona on long high voltage transmission lines and unfortunately they have not covered [68] the region of the most intense corona that precedes the flash over, conditions existing in electrical precipitation. The voltage on a line (V), the voltage at which corona starts (V_0) and the power loss (p) in watts are given by the expression following:

$$p = c^2(V - V_0)^2 \tag{15}$$

where c is a constant and V is not greatly beyond the value of V_0. For alternating or intermittent values of V the corona is "pulsating," starting when the voltage reaches V and stopping when it falls a little below V. This pulsation produces a cyclic change in the line admittance [69] and causes distortion in the current and voltage wave forms.

For alternating currents the corona causes harmonics, especially the third. In transmission lines corona harmonics present several serious problems.[70] In electrical precipitation the use of a mechanical Lemp rectifier increases the abruptness of the pulsations and severely stresses the insulating parts of the system.

The electrical precipitation problem requires the corona laws for several gases as well as for air, for these gases at relatively high temperatures and in various mixed proportions.[71] Eventually the properties of an electrical precipitator will be sufficiently well known to express in terms of equations in which the readings of switchboard instruments will suffice to give the determining factors.

(g) In the case of a "free" particle of mass (m) Newton's law for a force Fm acting upon the particle is to cause the particle to acquire acceleration (ρ) in the direction of Fm. In an electric field of intensity (E) a particle with an electric charge (xe) is acted upon by an electric force (xEe). Between collisions the charged particle is "free" to move in the direction of E.

$$Fm = m\rho. \qquad xEe = m\rho. \tag{16}$$

The Brownian movement indicates how the "free" straight-line motion of small particles is destroyed at the end of each collision. Small and essentially spherical particles follow Stokes' law as expressed in equation (7). When the particles are larger, such as "drops" or bubbles, the law is again modified especially when the shape is a variable. In the case of a bubble [72] rising in water the bubble attains a constant terminal velocity almost immediately and traverses a helical path with the long diameter of the bubble normal to the path. There is a maximum velocity of 27.8 cm./sec. for a bubble of radius 0.165 cm. With the axis of x upwards, ρ the density of water, Vv the volume of the bubble, φ and K resistance coefficients,

$$kg\rho V_v = \rho V_v \frac{d^2x}{dt^2} + k\varphi \left(\frac{dx}{dt}\right)^2 \tag{17}$$

The most fundamental work on electrical precipitation has been that on "slow-motion" precipitation by Millikan. When this work is done under high voltage conditions electrical precipitation as now applied in industry will have become an exact science.

(h) If the V's and Q's of a corona are plotted as rectangular coördinates the relation between VQt where t is the time is a closed curve of the period of a cycle of the alternating current and the area of the VQ curve is a measure of the corona loss of energy per cycle. Hesselmeyer and Kostko [73] use a cathode-ray cyclograph to produce the VQ curves on a fluorescent screen. As the positive and negative coronas differ the VQ curve is not symmetrical to the axes. The VQ curves with barriers placed between the active and passive electrodes indicate the effect of these on the space charges.

(i) Many investigators have studied the effect of "conditioning" the suspensoid gases either before or during their passage through the precipitator. "Conditioning" includes the regulation (lowering) of the temperature, the addition of water vapor either as a spray or as a vapor or steam, the addition of chemicals such as acids, the addition of clay, sand or other material, etc. Numerous patents on conditioning have been issued. Undoubtedly "conditioning" is a valuable aid in precipitation but the added attention, complexity of apparatus and cost must also be considered.[74]

(j) The current in an electrical precipitator is of somewhat the form [75]

$$I = A_8 \frac{(V - V_o)\,V}{V_s - V} f_1 (f) \tag{18}$$

where V_o is the voltage at which corona starts, V is the impressed voltage and V_s is the voltage of flash over. A_8 is a term that is very complex in general, depending upon the kind, temperature, velocity and pressure of the gas (M), the nature and the condition of the suspensoid (S), especially as regards its electrical properties and the condition of the electrodes (p_-, p_+) as regards their shape, the amount of precipitate formed on them, etc.

$$A_s \equiv f_2 (M),\ f_3 (S),\ f_4 (p_-, p_+). \tag{19}$$

In power (P) measurements on corona loss at a frequency (f) and with a capacity (C) from the conductor to neutral, Henline and Ryan [76] give a formula,

$$P = 4fC\,(V^2 - VV_o). \tag{20}$$

where the f_1, f_2, f_3, f_4 are functions of conditions that will be determined by future research.

In electrical precipitation work it appears best to keep the voltage at a maximum as near V_s as possible. The development of the Girvin generator was made with this end in view. The presence of high frequencies and occasional spark over may have some value however in the ionization process and maintaining the electrodes so that they can carry I. The effect of (f_1)[77] is such that the space charge type of corona structure disappears at a frequency of about 5,000 cycles for air under n.p.t.

From equations (8) and (13),

$$\log \frac{R}{r_o} = \log \frac{R}{a} - \log\,[1 + b/a\,(V - V_o)] = \log \frac{R}{a} - \frac{b}{a}\,(V - V_o) \text{ approximately.}$$

and

$$I = \frac{2KV(V - V_o)}{R^2 b/a(B_1 - V)} \tag{21}$$

This equation for I gives values of K that are of the right order of magnitude for clean gases. The formula for I for an electrical precipitator should explain the "peculiarities" that happen in electrical precipitation so that the electrical instruments with a knowledge of the suspensoid should describe the operation of the precipitator.

(k) The physical and electrical properties of the precipitated suspensoid affect the operation of a precipitator in numerous ways. ZnO forms almost a continuous dielectric, causes intense space charges both on the ZnO and in the gas and thus chokes down the corona. The addition of moisture or acid such as SO_3 aids the precipitated material to give up its charge to the collecting electrode. From 0.1 to 0.4 horse power is used per 1,000 cu. ft. of gas treated per minute. The gas velocity ranges from 2 to 25 ft. per sec. through the treater with averages around 5 to 7 ft. per sec.

(l) It is urged that no better way of teaching electricity and chemistry can be devised than the treatment of the basic principles that are involved in the ideally simple electrical precipitator consisting of a wire axially placed in a conducting cylinder. The phenomena can be described in terms of the basic conceptions of electromagnetism.

In an electrical precipitator corona starts around the active electrode when there are about 1,700,000,000 electrons per sq. cm. of surface and the surrounding intensity of electric field is about 30,000 volts per cm. The gradient about the passive electrode is then about 1,000 to 2,000 volts depending on the shape and size and the amount of charge held by the precipitate. About 300,000,000 electrons are required to raise a foot length of precipitator 1 volt. Only a few ions are "used" to charge suspensoid particles. Formulas can be derived describing "clearance," "precipitating force," "efficiency," the "tracks" of the suspensoid particles, the "time" and the energy required, etc. (*See* the author on "Precipitation," Vol. II, Bogue's "Colloidal Behavior.") These "electrical" methods of viewing phenomena are rapidly becoming the basic way of describing all chemical phenomena.

(m) In the Oski electrical precipitator, reinforced concrete electrodes are used for collecting the dust. The power consumption is thus slightly lowered and danger of arc-over is reduced. Six watt-hours of electrical energy will clean 1,000 cu. ft. of fume.

(n) Electrical precipitators sufficiently large to clean 2,000,000 cu. ft. of fume per minute have been built. Several thousand installations of various sizes (including about 2,000 in Europe) have been made.

(o) For the automatic control of an electrical precipitator, *see* P. B. Harwood, *Iron Age,* **118,** 1345-6 (1926). For a discussion of the physical principles of electrical precipitation, *see* R. Seeliger, *Siemens Z.,* **7,** 1-6 (1927); *Iron and Steel Eng.,* **6,** 143-6 (1929).

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[15] R. V. Wood. *Glass Ind.*, **4**, 106-7 (1923).

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[17] F. Bordas, *Tech. sanit. munic.*, **17**, 56-60 (1922). $Ca_3(PO_4)_2$ was ground to 0.001 mm. diameter and inoculated with *Micrococcus prodigiosus*. This dust was completely sterilized in a 30,000-volt precipitator. Most odors were destroyed on passage through the precipitator. O_3 is removed by passing it over rubber.

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[22] d'Arsonval, Bordas and Touplam, *Compt. rend.*, **170**, 636 (1920); *J. Ind. Hyg.*, **1**, 323 (1919).

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[25] *See* W. W. Strong, Chapter XXIII, Vol. II, p. 546. Bogue's "Colloidal Behavior," New York, McGraw-Hill Book Co., **1924**.

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[27] *Sci. American*, **128**, 224 (1923).

[28] Much of the fog and smoke lies comparatively close to the ground and could be removed from city air if it is found that ultra-violet light is a necessity in city sanitation and that artificial ultra-violet light is not suitable. Like rain production, this application of electrical precipitation could only be practicable under very special conditions.

[29] U. S. Pats. 1,071,532 and 1,096,765 (Strong). *See* the "Corona Voltmeter" by J. B. Whitehead in various numbers of the *Proc. Am. Inst. Elec. Eng.* In 1915 and 1916 the writer developed a voltmeter based on the increased gas pressure produced in the corona. Such a corona pressure voltmeter was used on a Girvin high voltage generator at a Chemical Exposition Exhibit at the Grand Central Palace, 1917. The "electric wind" and corona pressure effects were both employed to indicate conditions in the electrical precipitator and to measure corona chemical reactions. A similar use of the electric wind has been made by Kegerreis, *Phys. Rev.*, **4**, 762 (1924).

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[37] du Noüy, *Phys. Rev.*, **23**, 556 (1924).

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[63] Strong, *J. Franklin Inst.*, p. 262, Sept. 1912.

[64] U. S. Pats. 1,070,556, 1,071,532, 1,096,765, 1,325,124; British Pat. 21,199 (1913).

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The Super-Centrifuge in Industry

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Centrifugal machinery, mainly of the hydro extractor and the bottle centrifuge type, has been used in industry for many years. Both the above-mentioned machines are of the non-continuous or batch type. Except for their use in the dairy industry, high-speed centrifugals for the solution of industrial problems remained relatively unknown until recently. The super-centrifuge was developed in response to a demand for equipment to handle many problems for which gravity settling or filtration are unsatisfactory or impossible.

The industrial applications in which the super-centrifuge is used fall roughly into two classes: (1) Separation of solid from liquid, or clarification; (2) resolution of emulsions of two immiscible liquids, or separation. It will be convenient first to treat of the former classification.

Separation of Solid from Liquid.

For a clear understanding of the work performed by a centrifuge, the phenomenon of gravity settling should be reviewed in brief. If a system consisting of a suspension of water and coarse solids, such as ferric oxide or silica, is allowed to stand, the two components will separate into sharply divided layers, whose relative positions in the containing vessel will be in the order of the magnitude of their respective specific gravities.

Stokes' Law

$$V = \frac{2r^2 \times (S - S')a}{9\eta}$$

where V = velocity of settling, r = radius of the suspended particle, S = specific gravity of the suspended particle, S' = specific gravity of the continuous phase, a = the accelerating force, η = the viscosity of the continuous phase, illustrates the influence that the viscosity of the continuous phase, the size of the particle, and gravity differences play in determining the rate of separation.

If the accelerating force is gravity, a becomes the gravity constant, and V will have a definite value. But if a is a high centrifugal force equal to many thousand times the force of gravity, the value of V will be correspondingly increased. When a suspension is subjected to centrifugal force by passing it continuously through the rotor or bowl revolving about a vertical axis, centrifugal force acting outward from the center of rotation, causes the denser of the two components in the system to move towards the periphery, and to collect against the wall of the bowl. Thus, if the specific gravity of a suspended solid be greater than that of the dispersing medium, the solid will be found in a compact mass adhering to the wall of the rotor. Should, however,

the specific gravity of the suspended matter be less than that of the dispersing medium, it will be found at a point near to the axis of rotation, and will collect in a column on the inner surface of the rotating liquid.

Where the suspended matter of a two-phase system is so finely divided as to exhibit Brownian movement, the tendency of the disperse phase to distribute itself uniformly throughout the continuous phase is opposed by the force of gravity and an eventual equilibrium is obtained. From a practical point of view such final distribution does not constitute a separation, for the disperse phase should be concentrated in a small fraction of the continuous phase, and the latter obtained substantially free from suspended matter.

If a system which has reached equilibrium be subjected to high centrifugal force, the equilibrium will be altered and in many cases practical separation as defined above be obtained. Thus the super-centrifuge is capable of separating suspensions which will not separate by gravity under any condition.

Ayres [1] has suggested an interesting analysis of the question. He finds that in a suspension containing 1 per cent of solid, subsidence under gravity will occur when the product of the effective mass of the particles (volume $\times$ difference between the densities of the disperse and the continuous phase) in grams and the constant 10^{-17} equals 10. When this product is less than 10, only partial settling will occur.

When centrifugal force is applied to such a suspension, separation is complete if the product of the effective mass, the force in dynes and the constant 3×10^{-16} is greater than or equal to 10. Under conditions where the product is less than 10, only a partial separation will occur.

The commercial super-centrifuge accomplishes its separations in times varying between $6\frac{2}{3}$ minutes to $3\frac{1}{2}$ seconds, with an average period of 25 seconds as the time which a unit volume of liquid remains in the bowl. The lower figure corresponds to a throughput of 10 gallons per hour, used in the recovery of *Bacillus acidophilus* from broth, and the higher to a throughput of 1,200 gallons per hour, used in the dehydration of transformer oils. The super-centrifuges used in industry operate usually at 15,000 r.p.m., to deliver a separating force of 13,200 times the force of gravity. The super-centrifuge for laboratory use operates at 40,000 r.p.m. and delivers a maximum centrifugal force of 42,000 times the force of gravity. Bearing in mind the fact that these centrifugals are constructed of material with a large factor of safety and whose tensile strength is accurately controlled, it is evident from the foregoing that the field of their application must of necessity be wider than that of centrifugals operating at low speeds and delivering only a fraction of the centrifugal force possible with a super-centrifuge.

The super-centrifuge (Fig. 1) consists essentially in a suspended tubular rotor or bowl, supported with suitable bearings. The liquid to be treated is either pumped or fed by gravity at the desired rate into the bottom of the bowl, and after passing upwards in a hollow column, it overflows into the covers and out of the cover-spout, whence it runs by gravity into any suitable receiving container. If an emulsion is being resolved, the light liquid is discharged into one cover and the heavy liquid into another. Solids are retained in the bowl.

In practice, the results obtained with the super-centrifuge are dependent on a number of factors, the most important of which is the effective mass of the particle. Effective mass may be defined as the product of actual mass by the difference in specific gravity between the continuous and the disperse phase.

Hardly less important is the viscosity of the medium through which the particles of the disperse phase must move. Such viscosities may be so great

as to cause the rate of subsidence under centrifugal force to be beyond practical limits. In many cases, however, effective mass of the particle may be increased, or the viscosity of the continuous phase decreased, by dilution, or by raising the temperature.

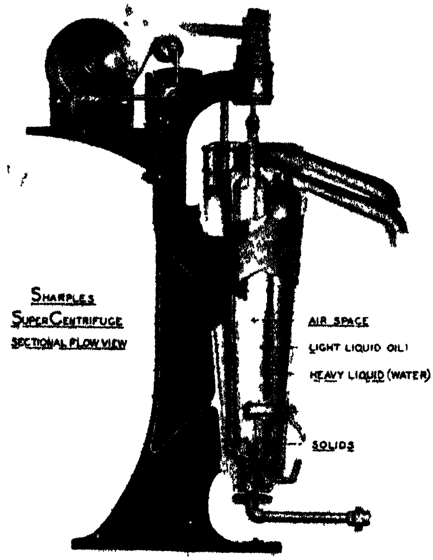

FIG. 1.

The effect of reduction in viscosity through increased temperature upon efficient centrifugal clarification may be clearly illustrated by the accompanying curves (Fig. 2). It should be noted that the viscosity of a petroleum oil is reduced by approximately 30 per cent for each 10° F. increase in temperature.

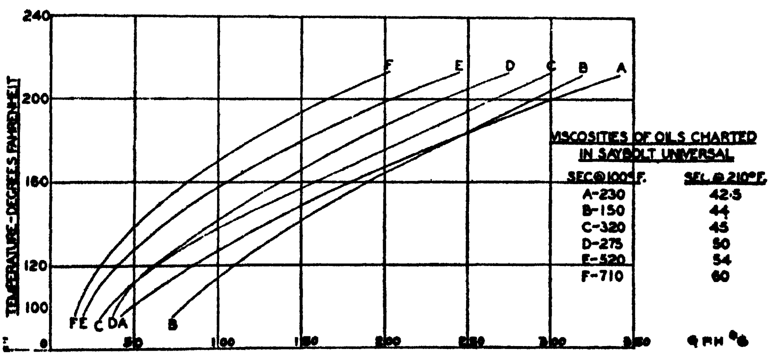

FIG. 2.—Capacity temperature chart for representative lubricating oils.

Six lubricating oils representing as many standard brands, and all badly carbonized and contaminated were chosen, and the capacity in gallons per hour at which effective clarification was obtained plotted against the temperature of centrifugation.

Reduction in viscosity by heating to allow gravity settling of the suspended particles is frequently impractical, on account of convection currents which oppose subsidence. Convection plays no part in the rotor of the super-centrifuge. Furthermore, the cost of heat applied over a long period of time is very often found to be prohibitive. Where a perishable product is being handled, gravity settling with or without heat is ruled out on account of deterioration during the time required for subsidence.

There is one class of dispersoid which is extremely difficult to sediment completely with a super-centrifuge, although it will settle rapidly by gravity. A typical example is freshly precipitated ferric hydroxide, in which subsidence is accompanied by agglomeration. When such a suspension is passed through the super-centrifuge, unless actual coalescence has occurred, the suspended particles are partially deflocculated and will deposit in the bowl only in part. If the effluent from the centrifuge is allowed to stand, agglomeration will again take place, and a certain amount of solids will precipitate.

Such suspensions containing flocculent solids are not altogether impossible to handle centrifugally. In the manufacture of certain jellies, the fruit juice will settle to about 85 per cent of clear liquid and 15 per cent of flocculent suspension. If 100 gallons of juice is passed through a super-centrifuge, approximately two gallons of pasty solid and 98 gallons of opalescent liquid are obtained. The effluent on standing will settle to 98 to 97 per cent clear liquid and 2 to 3 per cent sludge, which latter is mixed with another batch to be centrifuged. The net result of the operation is a saving of some 13 per cent of brilliant product over and above the amount obtained by the old method of gravity settling.

The sedimentation of *Bacillus acidophilus* from broth culture furnishes an interesting example of the ability of the centrifuge to remove finely divided solids. The bacilli, which vary in length from 1 μ to 3 μ, and have a diameter of approximately 0.5 μ are formed in the broth culture under carefully controlled conditions. When the concentration of the bacilli has reached fifteen hundred million per cubic centimeter, the broth is ready for centrifugal treatment. It is fed through a battery of super-centrifuges at the extremely low rate of 10 gallons per hour, and the effluent, whose bacterial count has been reduced to twenty-five million per cubic centimeter is wasted. When the centrifugal rotors are opened, the bacilli are found adhering to the wall of the bowl in a putty-like mass. From this form they are worked up into a special preparation, providing extremely high bacterial concentration.

Filter presses and centrifuges are both used for removing solids from liquid, but they are not interchangeable. Each has its field of most effective operation, depending upon the difference in action, and the individual material to be treated.

The efficiency of a filter press depends upon the deposition of the solids on the face of the filter cloths, in such form as will permit continuous flow through the cake thus built up. If the solids are slimy they will quickly clog the pores of the cloths, raise the pressure and frequently break open the press. The centrifuge is open to none of these objections, since the solids are collected against the wall of the bowl and a clear liquid flows away from and not through the mass of separated solids. A good example of this type of problem is the removal of finely divided solids from heavy varnishes, which are difficult to filter, but which are readily clarified on passing through the super-centrifuge.

When suspensions are treated in the super-centrifuge in which a certain portion of the dispersed solid is an extremely finely divided state, centrifugal

force will remove the coarser material, and leave the very finely divided solid suspended in the disperse phase.

Such an application is found in the manufacture of pigmented lacquer and enamel. In ordinary practice it is necessary to grind the pigment to an extreme state of fineness in order to avoid rough spots on the finished article, and in certain plants this degree of fineness is obtained only after approximately 28 hours grinding, although at the end of 8 hours, 99 per cent of the suspended pigment has been reduced to the desired size. If such an 8-hour batch of enamel or lacquer is passed through a super-centrifugal, operating at fairly high capacity and slightly reduced speed, approximately 3 per cent of pigment will be removed. The finished product will give a perfectly smooth and glossy surface, and in addition the suspension of the pigment in the vehicle will be considerably more permanent than in the case of longer grinding without centrifuging.

A common practice is to add approximately 3 per cent more pigment than normal, grind for 8 hours, and then clarify with the super-centrifuge. The resulting product, which contains exactly the right amount of pigment, is of a better grade than can be obtained by the old system, and in addition the capacity of the plant is greatly increased.

The Centrifugal Treatment of Emulsions.

An emulsion may be described as a stable mixture of two immiscible liquids, which for convenience we shall designate as oil (A), and water (B). Either A or B may be the continuous phase, hence, there are two possible types of emulsion, oil-in-water or water-in-oil.

Pure oil and pure water will emulsify only with the greatest of difficulty, and when a stable emulsion is finely formed after prolonged agitation in a shaking machine, or by refluxing the two liquids together, it contains only a very small proportion of the disperse phase.[2] However, should a third substance be present which will act as a stabilizer, it is possible to suspend large quantities of water in oil or of oil in water. Certain naturally occurring stable emulsions of salt water suspended in crude petroleum contain as high as 70 per cent of the disperse phases. These stabilizing substances are known as emulsifying agents and their ability to dissolve in, or be wetted by one of the liquids, determines which shall be the continuous and which the disperse phase.

Sodium salts of fatty acids, or soaps, will stabilize an emulsion of oil in water. If a dilute soap solution be agitated with oil, the soap tends to concentrate in the interface between the oil and the water. The surface tension between the water and the emulsifying film is lower than the surface tension between the oil and the emulsifying film, and therefore the interface will tend to curve so as to be convex on the water side and we therefore have an emulsion of oil-in-water.[3] The protective film effectively prevents the coalescence of the oil globule. If sodium chloride is added to such an emulsion, the electrolyte precipitates the soap, thus breaking the protective film, and the oil globules coalesce, destroying the emulsion.

If instead of sodium chloride, calcium chloride be added to the aforementioned emulsion, the oleates will be precipitated as calcium soap, and if such precipitation be carried to completion, the emulsion will be reversed, since the calcium soaps, being soluble in the oil, will lower the surface tension between the protective film and the oil and cause the interface to become concave to the water. Again coalescence is prevented by the presence of the calcium oleate in the protective film, and a stable water-in-oil emulsion results.[4]

Other emulsifying or stabilizing agents are glue, gelatin, gum arabic, albumen, etc., which promote the suspension of oil-in-water, while finely divided carbon, clay, asphaltum, and naphthenic acids stabilize emulsions of the opposite type.

Bearing in mind the foregoing, it is at once obvious that the resolution of emulsions under centrifugal force consists in two distinct steps, (1) the subsidence of the suspended particles of the disperse phase, and (2) coalescence of these particles after subsidence

Subsidence in emulsions follows Stokes' Law and the effect of centrifugal force is the same as that outlined for a suspension of solid particles in liquid, but coalescence is a different matter altogether, for it depends upon the removal of the adsorbed film surrounding the individual globule. Should the emulsifying agent be sodium oleate, in sufficient quantity, the greatest centrifugal force as yet developed either commercially or in the laboratory will be found to be inadequate to cause its subsidence.

Therefore, it is necessary to weaken or destroy protective films which are due to substances of molecular dimensions, through the aid of chemicals, before the super-centrifuge can effect satisfactory coalescence.

As an example, consider the Sharples process for the recovery of neutral oil from soap stock or foots produced by the caustic soda refining of vegetable oils.

The soap stock settles in the form of a thick gel, in which is dispersed from 25 to 30 per cent of refined oil. If the gel is heated to such a point that it will flow and is then subjected to centrifugal force in the rotor of the super-centrifuge, no oil will be separated. When, however, the soap concentration is reduced to 20 per cent of its former strength by diluting with four parts by weight of water, the super-centrifuge will recover 60 to 65 per cent of the emulsified oil in the form of a thick cream containing 75 to 80 per cent oil in which soap water is the continuous phase.

Further centrifugal treatment of this cream will not cause it to coalesce, even when a batch is whirled at a speed of 40,000 r.p.m., but the addition of a small amount of saturated sodium chloride solution will precipitate the soap, and so weaken the emulsion that when the mixture is centrifuged in the commercial super-centrifuge, a clear neutral oil and a practically oil-free effluent are discharged at a relatively high capacity. The precipitated soap is discharged with the water in flocculent masses.

In cases where the emulsifying agent is a finely divided solid, the super-centrifuge can usually effect subsidence and coalescence in a single operation.

The oil can be recovered from spoiled mayonnaise dressing by simply heating the emulsion and passing it through the centrifugal. Clear oil and clear vinegar are discharged, while the emulsifying agent, in this case the powdered yolk of eggs, is retained on the walls of the bowl.

The super-centrifuge has proved exceedingly valuable in the rapid dehydration of oils which occur industrially in emulsions with water, and which, if the force of gravity is depended upon, either deteriorate through contact with the aqueous phase at the temperatures and during settling periods which are necessary for gravity subsidence, or are partially lost through evaporation under similar conditions.

For example, in the production of fish oil, the fish are first cooked with steam and then pressed in a screw press. The effluent contains fish meal, oil and water. If the liquid from the press is allowed to settle by gravity, a certain amount of the oil is lost with the waste water, the prolonged standing causes the free fatty acid content of the oil to increase rapidly, and its color darkens.

By centrifuging the press liquor immediately, a clear light oil of low, free fatty acid content is obtained, and the yield is considerably increased, since the water discharged from the centrifugal contains much less oil than the effluent from the best type of gravity separator.

Another instance is the dehydration of crude petroleum. The oil as pumped from the wells contains a considerable quantity of emulsified salt water, the stabilizing agent being finely divided clay. The emulsion may be concentrated by gravity settling in tanks equipped with heating coils, but such procedure entails the loss of some of the light ends from the oil, and requires a large amount of steam. The super-centrifuge is not only able to produce a satisfactory pipe line oil, but at the same time resolves the greater part of the emulsion, which settles out under the influence of gravity, by causing subsidence of the stabilizing agent. The operation is much more rapid than the old method, and evaporation losses are reduced to a minimum.

An interesting application of the super-centrifuge, which involves the continuous discharge of wax-like solids, is found in the dewaxing of lubricating stocks. Steam cylinder stocks which are used to give body to motor oil, when filtered to colors acceptable to the trade, will solidify at relatively high temperatures. Solidification is due to the presence of amorphous wax or petrolatum, and in order to produce a lubricant which will remain liquid at low temperatures, the wax must be removed.

Formerly such removal was accomplished by dissolving the stock to be dewaxed in light gasoline, and then slowly chilling the solution in large insulated tanks equipped with brine coils. The wax or petrolatum precipitated from the gasoline solution at low temperatures and gradually settled to the bottom of the tanks. The supernatant, relatively wax-free oil was drawn from the upper parts of the tank and the solvent removed by steam distillation until the original flash and fire of the oil were restored.

The method was open to the objections of long settling periods, occasional failure of the wax to precipitate in a satisfactory form, high refrigeration costs, and relatively low yields of oil (70 per cent). The oil produced showed a pour test in the neighborhood of 40° to 50° F. and could not, in consequence, be used in large quantities for blending low cold test oils.

If a chilled suspension of wax in cylinder stock-naphtha solution is centrifuged, the wax will collect in the rotor of the centrifugal and clear oil will discharge, but unless extreme care is taken, it is almost impossible to discharge the wax satisfactorily. However, through a special design of the centrifugal rotor and the use of a carrier liquid, heavier than the wax and immiscible with the oil naphtha solution, it was found possible to discharge the wax continuously and to produce a bright stock which after reduction shows a cold test in the neighborhood of 15° F. The chilling period, and in consequence refrigeration costs, were greatly reduced and the yield of bright stock was increased to 85 per cent.

Further design and experimentation brought to light the fact that "long residuum" (i.e. still residue which contains all of the lubricating stocks in a given crude) could be handled by the centrifugal dewaxing process to yield a dewaxed low cold test oil. Formerly the only method of dewaxing such residuum had been the cracking of the wax to a crystalline structure and pressing with a resultant loss of some 30 per cent of the lubricating oil. "Long residuum" would not dewax by the cold settling process.

Centrifugal dewaxing has been extended further to cover the treatment of various heavy distillates in which, by careful control, the wax has been carried over in the amorphous form. To-day more than 10,000 barrels per

day of oil dewaxed centrifugally are being produced in the refineries of the United States.

It would not be difficult to multiply the instances of the application of the super-centrifuge to industrial problems, but those outlined above may be considered as typical. However, the following list will serve to give an idea of other important problems which have been readily solved by the installation of super-centrifugal equipment: The Continuous Purification of Dry Cleaner's Solvent; The Reclamation of Used Car Journal Oil; The Dehydration & Restoration to High Dielectric of Transformer Oil; The Continuous Clarification of Lubricating Oil in Service; The Reclamation of Cutting Oil; The Purification of Diesel Fuel and Diesel Crankcase Oil; The Degumming of Vegetable Oils; The Clarification of Clear Nitrocellulose Lacquers; The Dehydration of Coke Oven Tars; The Recovery of Silver from Waste Motion Picture Films; The Clarification of Barium Sulfide Solution; The Recovery of Cocoa Butter from Spoiled Chocolates; The Clarification of Caustic Soda Solutions; The Continuous Purification of Wool Scouring Liquor; The Dehydration of Light Asphaltic Oils; The Resolution of Refining Emulsions of Lubricating Oils and Caustic Soda; The Clarification of Fruit Juices; The Clarification of Pharmaceutical Preparations; The Recovery of Serum from Defibrinated Blood; The Reclamation of Used Circuit Breaker and Switch Oil. The field for the high speed, continuous centrifugal is continually broadening, and unquestionably the next few years will witness the successful solution of many difficulties, and the development of new industrial processes through the proper understanding of the part which can be played by high centrifugal force.

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Notes on Filtration, With Special Reference to Metafiltration

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Filtration may be defined as the removal of suspended particles from fluids during passage through a pervious medium. This definition covers the removal of suspended particles of liquids as well as solids both from gases and from liquids. There is no reason why the term filtration should be confined to the ordinary case of the removal of suspended solid particles from liquids.

This definition covers all the cases which can strictly be called filtration, but in actual practice especially in commercial work, processes of filtration usually or often involve purifications from matter which is not suspended, and may actually be dissolved. The removal of matter in this way is accomplished by making use of the property of adsorption which is possessed in varying degree by practically all substances.

It has been known as a matter of practice for many years that filtrations through certain materials produce desired effects, whereas filtration through other material, although perhaps this may be finer in its structure, is ineffective. A familiar example of this is the use of paper pulp for the filtration of gelatin. This medium effects a clarification which cannot be obtained by filtration through plain kieselguhr, the reason being the surface action of the paper pulp. Filtration of sugar solutions through charcoal is another instance of the same kind, and water purification by filtration through carbon filters was known to be satisfactory long before it was known that bacteria removal was due to adsorptive action of the charcoal.

For filtration purposes adsorption may be regarded as a surface attraction. Particles, or even molecules, are held upon the surface of the filtering medium much in the same way, but on vastly smaller scale, that pebbles are held on the surface of a freshly tarred road; or perhaps as iron filings are attracted to a magnet. On this analogy it is easily understood that the effect is limited in degree, as it can have action only upon matter which is extremely close to the surface; and once the surface is covered, its capacity is exhausted.

The effects of adsorption are not confined to suspended particles only, but may act upon dissolved matter. There are border-line cases between solution and suspension, and this region is occupied by the colloids.

As colloids differ from coarse suspensions mainly in the size of the particles, it is to be expected that filters could be found sufficiently fine in texture to remove colloidal particles by mechanical action. Such are ultra-filters,* in which the pores are extremely minute. Ultra-filters, however, are still extremely delicate and difficult to handle commercially. Ordinary filters with a filtering medium of cloth or sand are useless for colloid removal, except in the case of extremely fine bed filters, such as are provided by metafilters. As a result, in many practical cases use is made of adsorption to remove colloidal particles.

* See H. Bechhold's paper on Ultrafiltration in Vol. I of this series.—J. A.

The mechanism of filterbed action may be briefly considered. It is known that to achieve a fine filtration with a bed of moderate openness, a considerable thickness must be employed. Assuming that the action of a filterbed is the same as the action of a sieve, there would seem to be no reason why the thick bed should produce any better results than a thin bed, although the improvement is known to be a fact. It would be natural to suppose that the action of thick beds in effecting an improvement, depends on increasing the number of opportunities for entanglement provided by the ramifications of the minute irregular passages which penetrate from top to bottom of the bed. Experiments in the writer's laboratory have conclusively shown that the material is in fact trapped in the corners and crevices formed by the touching of the particles which compose the bed. The actual penetration into the bed of the material which is being held back by filtration, may be very considerable. In the case of fine suspension consisting almost entirely of very fine particles, it will be found that a thick bed will produce clear filtrate for a time and afterwards allow some of the material to pass through, due to the available positions for the retention of the suspended matter becoming gradually filled, so that the channels are to some extent smoothed out. This seldom happens in practice, because suspensions usually contain particles of large size as well as minute particles, and the large particles are stopped near the surface of the bed and themselves constitute a filtering bed of still greater fineness.

As mentioned above, however, it is not sufficient in all cases to have a bed of great thickness to secure a proper clarification—gelatin filtered through pulp being a case in point. Actually it will be found that a considerable clarification can be effected in this case merely by thorough agitation of the suspension with pulp followed by subsidence, the upper layers of the liquid being then quite as bright (although they have not passed through the filter) as would be the case in an ordinary filtration. The same experiment carried out with silica produces a less satisfactory clarification, but if the nature of the silica is changed by precipitating upon it a minute quantity of aluminum hydrate, it then becomes equally or more effective in producing the same purification. This is due to the alteration of the surface action of the material. (Ultra-filterbeds are described by Bechhold in Vol. I, this series. J. A.)

Having discovered a material which is specifically correct for a given colloid filtration, it next becomes necessary to use it in the most effective manner, and this is generally found to be best accomplished by causing the liquid to pass through a bed of the filtering material. Beds of filtering material may be built up on a variety of supports, such for instance as cloth or wire gauze, but it is very necessary that the nature of the support should be extremely rigid. During most filtrations the pressure acting from side to side of the whole filtering medium varies, increasing towards the end of the filtration. If the bed is supported upon elastic or weak material, this gives way and causes rearrangement of the bed here and there, which may lead to the constituent particles themselves being to some extent carried forward and spoiling the clarity of the product. Furthermore, the tendency of such materials as cloth to become clogged after repeated use, is a serious drawback. The metafilter forms probably the most satisfactory basis for the building of fine filtration beds, and a brief description may not be out of place.

A metafilter surface consists of the bevelled edges of a number of strips or rings of metal or other impervious material forming a sub-structure which interpenetrates and reinforces the material which it holds, in such a way as to reduce to a minimum the possibility of any breaking down or rearrangement. One of the simplest forms of metafilter is shown in Figure 1:

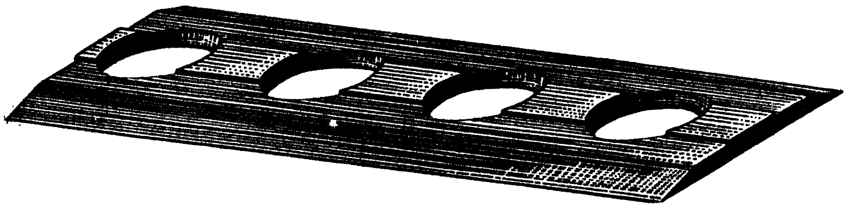

FIG. 1.—Metafilter strip—magnified.

It will be seen that the strip is flat on one side and the other side carries bevelled edges bordering a flat center. Along the middle of the flat center a rib of very small height is raised and perforations are made in the strip at regular intervals, the perforations being wide enough to overlap the rib but not wide enough to reach to the edges of the inner bevelled part. When many strips of this form are piled one upon the other, as in Figure 2:

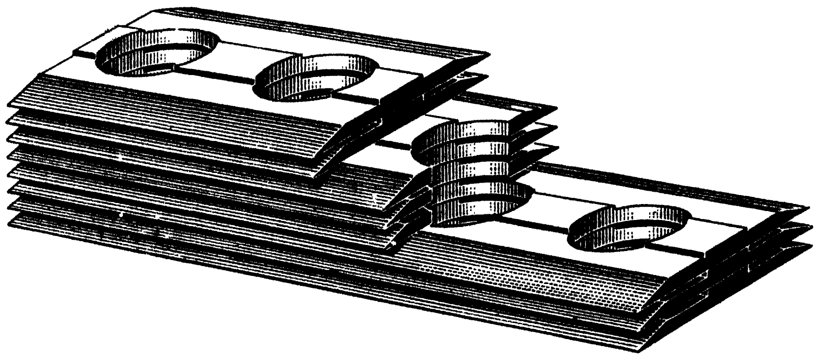

FIG. 2.—Magnified perspective view of metafilter assembly.

and held closely in contact, it will be seen that the perforations become superposed and constitute channels throughout the whole assembly, while the strips themselves are separated by a minute distance corresponding to the height of the rib. In actual practice the rib height is from one-thousandth to three-thousandths of an inch, these dimensions being sufficient to meet most practical cases. A part section of a complete metafilter filtering plate is shown in Figure 3:
The frame includes a bottom bar with a groove fashioned in its upper surface and leading to a spigot outlet. The metafilter strips are piled on this bottom bar, being held in position by grooves in the side rods, and the whole frame is completed by tightening down the top bar by means of the nuts. This closes the upper end of the drainage channels and brings all the strips into close contact. Filtration is accomplished by applying suction to the spigot and lowering the frame into the liquid to be filtered, or by enclosing the frame in a containing vessel through which the spigot projects, and forcing liquid into the vessel. It will be seen that a metafilter frame alone is only capable of comparatively coarse filtration, but when the V-shaped grooves on the surface of the frame have been filled with a porous filtering bed, as shown in Figure 4: it becomes capable of extremely fine filtration, as the liquid is forced to find its way through the fine filtering bed which is very rigidly retained in position.

To remove the filtering bed and clean the filter is an easy matter. Nothing but filterbed comes into contact with the actual strips and this is easily removed by backward flow from the inside of the frame, proceeding from the narrow to the wide end of the V-shaped channels, and thus avoiding any tendency for the bed to stick during removal.

It will not be necessary here to describe all the varieties of filtering members which can be built up of metafilter elements, but the same principle can

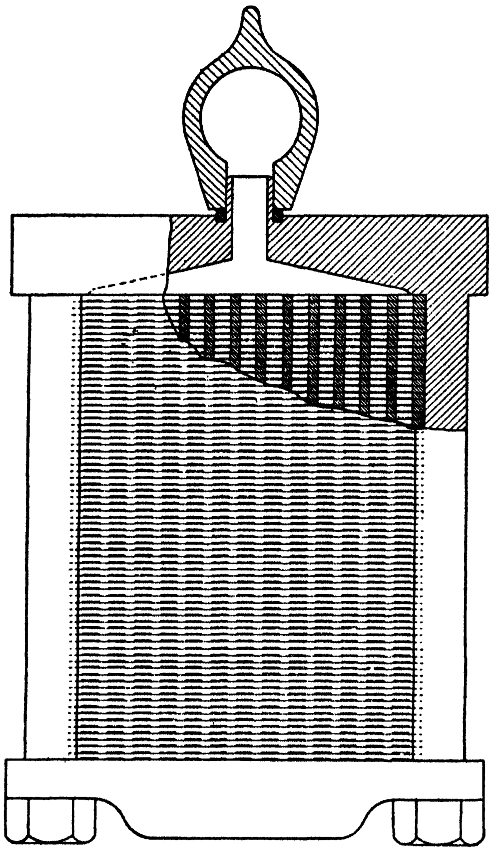

FIG. 3.—Metafilter in part section (filtering slits not to scale).

be made use of whether the metafilter itself is composed of long thin strips or rings or even of other geometrical forms.

Returning now to the general technique of the removal of suspended matter from fluids, it will be realized that this may be removed by different means according to its coarseness, and one may employ either settling, filtration, or adsorption, or a combination of two or more of these operations.

Settling may be very effective, but it depends on the size and weight of the particles to be dealt with and the time at disposal, and upon the depth of the liquid treated. If settling is extremely rapid, it may be very difficult to separate the material by filtration if the intention is to obtain the suspended matter in a solid cake. For instance, it would be very difficult to induce finely

divided lead or heavy sand to remain in suspension long enough to pump it into the interior of a filter press. Filtration is generally best for suspended particles of medium size.

In actual practice, it is often better to spend some time and trouble in getting the material to be filtered into the optimum condition, rather than to operate with a filter which is capable of removing it in its normal state. Such a treatment has a secondary advantage, for, if the particles are of reasonable size, not only are they individually more easily separated, but the accumulated cake which they form is more porous and consequently greater thickness can be dealt with; that is to say, a larger actual amount of material can be removed in one operation without cleaning the filter.

A well-known instance of the advantage of such treatment is presented by the filtration of barium sulfate. Barium sulfate, precipitated from moderately strong cold solutions, is extremely fine—the particles may be as small as one micron and even less, which is well within the colloid range. To remove barium sulfate of this degree of fineness, a very fine medium is necessary; in fact hardly anything except a fine metafilter or an ultra-filter will successfully cope with it. If, however, the precipitate of barium sulfate is formed by mixing hot solutions, one of which is added very slowly to the

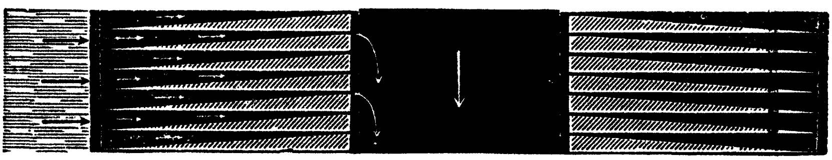

FIG. 4.—Transverse section through a metafilter with arrows showing course of liquids—magnified.

other, quite a coarse precipitate results which may be separated by almost any filtering material.

Another device which is also of considerable use in many cases is to form another precipitate in the already existing colloid suspension which has the effect of enclosing the colloid particles in itself, or perhaps, of attracting them to it. Well-known instances of this method of operation are the co-precipitation of aluminum hydrate or of calcium phosphate. The subsequent filtration of the large precipitated particles is an easy matter and these have already removed the colloid particles which would have caused a difficulty.

Another process which is very effective in many cases is to adjust the pH of the solution within narrow limits, which has the effect of inducing the suspended particles to coagulate, or perhaps to take on a crystalline form. The precise reason for the effect is not fully understood, but it is probably linked up with the interfacial tension of the particles and the liquid.* This process has been found particularly effective in the filtration of sugar solutions and of some organic phosphates.

The action of paper pulp in inducing clarification when stirred in a suspension has already been referred to and its effectiveness depends upon the facility offered to the smallest suspended particles to get right to the surface. The action is not quantitative as regards the amount of suspended matter, but

* An explanation which seems valid in some cases is that within certain pH limits proteins and other protective colloids are coagulated. It is not easy to obtain water free from protective (or coagulative) substances, as was pointed out as far back as 1840 by Ascherson. If a cumulative protective chain exists, the laming of one member might wreck the whole chain. *See* Vol. I of this series.—J. A.

depends upon the relative availability of surface to the smallest particles. It will be readily seen that comparatively large particles can only make point contact or, at the best, very small surface contact with the material, and consequently the effectiveness of the surface for retaining colloid particles is only slightly affected by the presence of large particles of the same nature.

Another effect which has to be carefully studied in some instances is hydrolysis. For instance, in the case of a precipitate of Prussian blue, or of ammonium phosphomolybdate, filtration can be easily accomplished so long as a certain amount of electrolyte is present in the liquid; but when the salts are removed and pure water follows on, the precipitates may go into colloidal solution and penetrate the filter.

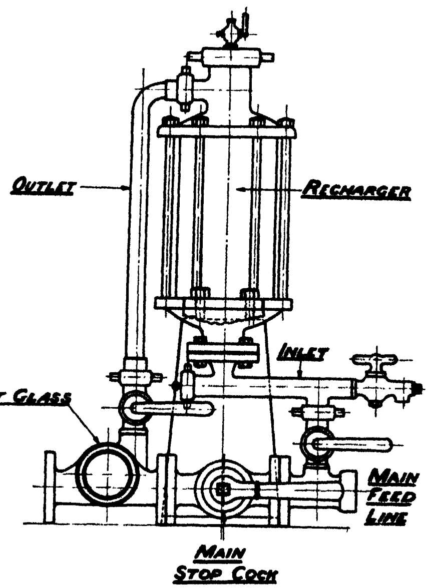

Fig. 5.

The use of filteraids, which are easily suspensible materials, usually of an open porous nature, is commonly employed in the case of precipitates which are themselves of soft and easily compressible nature. The mechanical basis of their action is a very simple one. It merely consists in increasing the porosity of the bed by separating the individual suspended particles by the open particles of the filteraid, which provide capillary passages for the liquid to pass through the bed between the gummy particles. Filteraids may also have a further action in coagulation as referred to above.

To obtain the best results with the addition of filteraids, uniform mixing in constant proportion is very necessary. This may be secured in many commercial operations by stirring together in a tank, but the constant addition of a powder in suspension to a liquid in a pipe is a matter of some delicacy and it may be of some interest to describe briefly a device which has been found very effective in adding filteraid to such materials as beer during filtration.

This device, which has been called a recharger for want of a better name, is illustrated in Figure 5.

In the illustration it will be seen that the main flow of liquid to which the filteraid is being added takes place through the large pipe at the bottom carrying a stop cock. The recharger constitutes a by-pass round the main control cock and consists of a vessel containing a strong suspension of the filteraid material with pipes entering the main stream, one on either side of the cock. A sight glass is provided on the delivery side so that the amount of powder

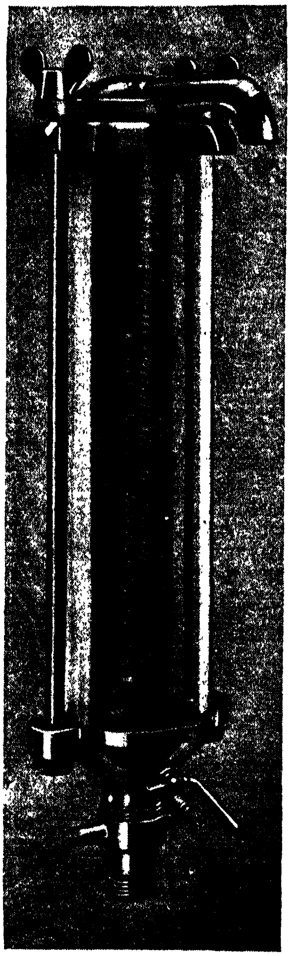

Fig. 6.

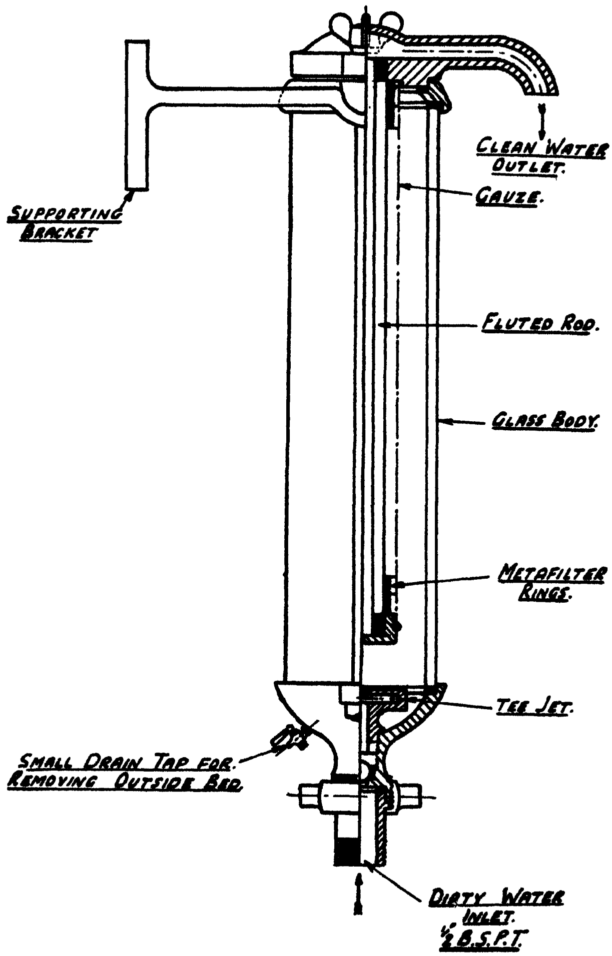

Fig. 7.

entering the stream can be inspected. To add filteraid by means of the recharger the stop cocks on the by-pass are opened, when part of the inflowing liquid passes upwards through the recharger vessel, carrying forward with it some of the filteraid, and rejoins the main stream from the pipe at the top of the recharger leading down into the sight glass. If larger quantities are required they are introduced by increasing the flow through the recharger, which is accomplished by partially closing the main supply cock. This

arrangement has been found extremely handy in use. It can be refilled without stopping the course of the filtration by closing the recharger cocks, emptying the vessel, and pouring in a further amount of filteraid suspension.

No general description of filters can be given here. The immense variety of forms and details necessitated by the different products to be dealt with, and degrees of purification desired, makes this impossible, but a fairly comprehensive description of many types is given in "Filtration and Filters." * The selection of a filter for the particular service in view must be decided by many different considerations. For instance, cost, availability of local labor, degree of separation required, the value of the product—whether the solid or the liquid, or both are required—whether solid is to be washed or not, whether continuous operation is necessary, and a host of minor considerations. The following two examples of filters, very different in type but both of which deal satisfactorily with colloid precipitates, are given as instructive examples.

The domestic water filter, shown in Figure 6, and in half section in Figure 7, contains some novel points which will repay consideration. In this filter the intention is to provide filtration through a filterbed of a high degree of fineness, making use at the same time of the effects of adsorption, and providing for renewal of the filtering surface without opening the filter or interfering with the clarity of filtration, so that long continued operation can be obtained.

The filter consists of a column of metafilter rings assembled on a fluted rod to provide drainage. The rings are not all of one diameter, but at small intervals over the length of the column rings of greater diameter are disposed. The object of this is to provide a good support for the filtering bed. Over the whole assembly is drawn a jacket of helically woven wire gauze and the assembly is screwed into the head of the filter. The body of the filter consists of a wide glass tube which makes joint top and bottom with the head and base of the filter. The base of the filter is conical in shape and contains a T-shaped admission piece with jets on the two branches disposed to give a rotary swirling motion to the contents. The filtering medium used is of special composition of such a nature as to precipitate aluminum hydrate very finely divided and intimately mingled with the general body of the material when mixed with water. The amount of filter aid used is adjusted precisely so that the filterbed is of such a thickness that it fills up all the spaces below the wire gauze, and in addition provides about the same thickness of the bed on the outside of the gauze. The arrangement is shown in section in Figure 8:

The filter is set to work by mixing the filterbed with sufficient water, pouring this into the glass container, then inserting the filter assembly and turning on the water. The bed takes up its position as just described, and filtered water leaves by the spout at the top. After a time, the slimy and fine-grained matter removed by the filter forms a skin over the surface of the bed, which if allowed to remain would slow down the working of the filter. At this point it is desirable to renew the surface, and this is very simply done as follows: The water supply is turned off from the filter and the small tap shown on the base of the filter is opened, and a small amount of the contents permitted to flow away. This has the effect of inducing a small flow of water backwards through the filtering element from the head, which detaches the filtering medium outside the wire gauze jacket, but leaves the inner bed unaffected. On restarting the flow, the detached bed is effectively stirred up and resuspended by the inflow of water and takes up its former position, but now the skin is disseminated throughout the mass and the porosity of the whole filter is in consequence very little affected. Filters of this type have been in use for many months without renewal of filterbed, operating effectively in germ removal throughout the time. A minor, but still important, point is that the whole of the filterbed is under observation the whole time, so that the operation of the filter can be well judged and the suspended matter removed. To renew the filtering medium altogether, the bed is accumulated on the metafilter support, then the filtering element is lifted out, washed clean by a small jet of water, and replaced with a new charge of bed.

* "Filtration and Filters," by J. A. Pickard, London, Ernest Benn, Ltd.

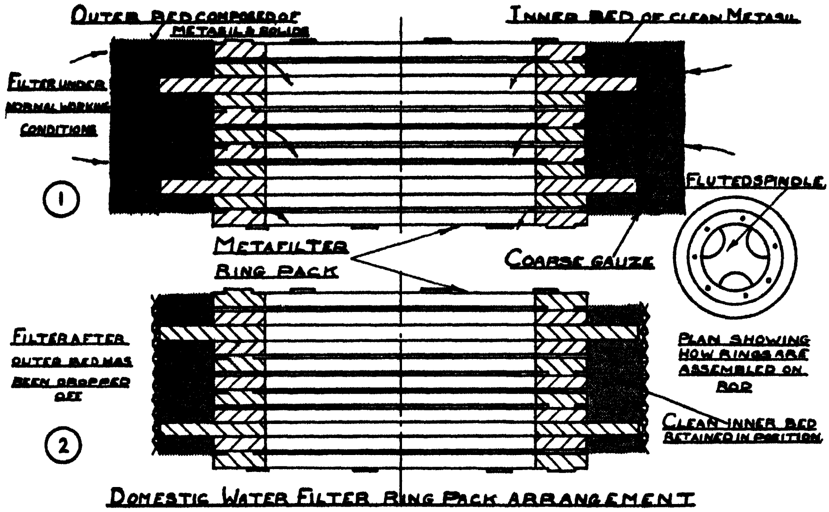

FIG. 8.

The second example is a filter of a much larger size intended to deal with transformer oil. It makes use both of adsorption, which in this case entails a certain time reaction, and very fine filtration. A typical plant is illustrated in Figure 9:

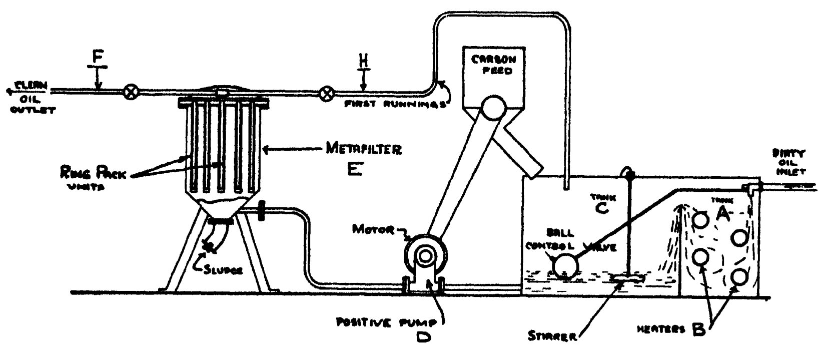

FIG. 9.

Transformer and switch oils may contain as harmful impurities water, colloidal carbon arising from arc quenching, and sludge. Suspended water may be removed by filtration but dissolved water and colloidal carbon require the assistance of adsorption to remove them. Sludge can be dealt with by a simple filtration if this is fine enough.

The oil enters the tank *A* first passing over electric heaters *B* which raise its temperature and reduce viscosity to the desired degree.* It then passes into compartment *C* where it is mixed with a special adsorptive filtering material, the composition of which has been arrived at after much painstaking work. The volume of oil in this tank is

* The filter normally operates at about 15° C., so that heating of the oil is necessary only to counteract wintry conditions, whereas apparatus formerly employed for this purpose requires the oil to be heated to 50° to 80° C.

adjusted so that the level remains nearly constant and so that the necessary time is occupied in passing through the tank which is required to secure the maximum benefit from the adsorptive action of the filteraid. The oil is withdrawn from this tank and delivered to the filter by a positively acting pump *D* and delivered into the body of the metafilter *E*. In this case the metafilter is also composed of ring packs which are suspended from the top division plate of the filter. In passing between the metafilter rings the filter material is separated and forms a bed on the outer surface of the filtering columns. The clean oil passes on and is delivered to the desired point by pipe *F*. Provision is made for recirculating the first runnings to the supply tank by means of the pipe *H*. The main advantages of this filter lie in its extreme simplicity, as it accomplishes by a straight forward pressure-actuated filtration, the removal of all three of the above harmful impurities, which previously has only been possible (if possible at all) by the combined action of centrifuging, paper filtration, and chemical treatment.

The filter is very simply cleaned by backflushing with a small amount of filtered oil through *F*, connections in practice being arranged so that this can be easily performed by means of the supply pump. The accumulated bed with the contained impurities slips easily from the surface of the filtering columns in long tube-like masses and slips out of the filter when the sludge cock is opened at the bottom of the funnel shaped base.

Despite extreme simplicity, metafilters of this type are found in practice to remove both colloidally suspended and dissolved water completely as well as colloidal carbon and sludge. Breakdown voltages are raised from any low level, say 10 to 15 kv on the B.E.S.A. specification, to 70 to 80 kv and higher.

The Flotation Process

By G. H. Buchanan,

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If we adopt the definition[1] that colloid chemistry is the "chemistry of bubbles, drops, grains, filaments and films," the process of concentration by flotation is properly classified as a technical application of colloid chemistry. It is, moreover, an application of great commercial importance, even when compared with the other great fields which the colloid chemist serves. Thus the tonnage of ore treated in the United States alone by this process amounted in 1929 to sixty million tons. At one metallurgical operation alone forty thousand tons of ore are treated daily.

Although concentration by flotation is not necessarily limited in its application to the beneficiation of ores, it is in practice so limited and in the present discussion it will be considered entirely from this viewpoint. It may be mentioned, however, that the process has possibilities of application to other industries, some of which have not yet been explored. As thus limited, the flotation process may be defined as a process for the separation of certain constituents of a complex ore mixture from other constituents, which depends upon the fact that certain of these constituents, notably the sulfides, attach themselves to oily bubbles while others fail to do so or do so only with difficulty.

In present day practice the process is usually limited in its application to the recovery of sulfides and of metallics. However, its application to the recovery of non-sulfides and of non-metallic minerals is increasing. It is quite possible that a monograph on flotation dated ten years hence will pay quite as much attention to the flotation of non-metallic minerals as to the flotation of sulfides. In the present discussion, however, we will merely list some of the non-metallic minerals which are now being recovered by flotation. Among these are rhodocrosite, phosphate rock, fluorspar, barytes, graphite and coal.

Nomenclature of Flotation.

The minerals recovered in the froth are usually, although not always, the more valuable constituents of the ore. There are occasional exceptions, as, for example, in the purification of tin concentrates. Here the pyrite, the more floatable mineral, is separated from the cassiterite and discarded. In general, however, the *concentrate* is recovered and the *tailing* is discarded.

According to early flotation practice only a single concentrate was made. When the ore contained only one floatable constituent this was satisfactory but when several floatable constituents were present it was necessary to rely upon other processes to separate the so-called *bulk concentrate* into its constituents. In some cases it was possible to make this later separation by a simple pyrometallurgical operation. For example, in the early days of copper flotation operators were quite content to recover the sulfide copper in a bulk concentrate with the sulfide iron, leaving the separation of copper and iron to the copper smelter. In other cases no adequate process was available for the

separation of the components of the bulk concentrate, making such concentrates valueless. For example, many complex lead-zinc ores could not be treated commercially by flotation because no method was known for separating the bulk concentrate yielded by flotation into individual concentrates of zinc and lead.

With the introduction of *differential* or *selective* flotation it became possible to treat such complex ores, separating by flotation the several floatable minerals not only from the *gangue* but also from each other. The nomenclature of this type of work is not uniform, but we may well adopt that suggested by Engineering and Mining Journal,[2] which limits *differential* flotation to processes in which only one concentrate is made, the other floatable minerals being discarded with the gangue. Flotation is said to be *selective* when more than one concentrate is made.

EXAMPLES FROM FLOTATION PRACTICE.

Before beginning our discussion of the details of the flotation operation it will be instructive to consider a few examples from modern practice which will show the nature of the separations which are being made.

Example 1.—This is a copper ore in which the copper occurs as chalcopyrite. The gangue is a heavy sulfide mostly pyrrhotite.

	Per Cent Copper
Feed	1.3 to 1.5
Concentrate	17 to 19
Tails	0.09 to 0.12
Per cent recovery	89 to 93

Example 2.—This is a complex lead-zinc ore from which three concentrates are produced. The assays of the various products are as follows:

	Per Cent Lead	Per Cent Zinc	Per Cent Iron	Per Cent Recovery
Heads	5 to 8	8 to 13	13	
Lead concentrate	68	5 to 18	4	93 to 95
Zinc concentrate	1.2	55 to 58	3 to 5	85 to 90
Iron concentrate	1.0	1.5	38 to 40	50 to 60
Tailings	0.5	0.8		

Example 3.—This is an example of excellent practice in the separation by flotation of a very small amount of copper occurring as chalcopyrite from an iron ore, principally magnetite.

	Per Cent Copper
Feed	0.64
Concentrate	28 to 30
Tails	0.06 to 0.09
Recovery	88 to 90

PREPARATION OF THE ORE FOR FLOTATION.

The first step in the preparation of the ore for flotation is the grinding operation, and the degree of comminution required depends upon the intimacy of association of the constituents which are to be separated. Too coarse grinding yields low grade concentrates and low recoveries and the tendency in modern flotation is toward finer grinding. However, over-grinding is undesirable, not only because of the cost of the extra grinding, but also because over-ground minerals are difficult to recover by flotation. In the operation

of the Utah Copper Company, the largest in the world, the grinding is approximately 70 per cent through a 200-mesh sieve.

For ideal flotation conditions the sulfide surfaces should be unaltered. Flotation is essentially a surface phenomenon and sulfide particles with altered surfaces are more difficult to float than freshly broken minerals. Some ores are peculiarly subject to alteration and even a few days in stopes or bins are sufficient adversely to affect their flotation behavior.

THE EQUIPMENT OF FLOTATION.

Extended discussion of the equipment of flotation is outside the scope of the present paper. Shown below is a flow sheet taken from a technical bulletin of one of the large manufacturers of flotation equipment [3] which may be considered typical. The flow sheet in question shows the selective floating of more than one mineral, such as is encountered in a lead-zinc ore or in a lead-zinc iron ore.

In the sketch, *A* is the *Ore Feeder* delivering ore at a uniform and predetermined rate to the *Ball Mill B* operating in closed circuit with the *Classifier E*. The ore pulp for flotation then passes to the *Conditioning Tank J* where are added to it the reagents required for flotation of the lead and depression of the zinc and other floatable minerals.

K is a ten-cell *Flotation Machine* of the mechanically agitated type. The incoming flotation pulp is delivered to the fourth cell of the machine. Clean lead concentrates are removed from the first four cells. The rough concentrates from the last six cells are returned to the head of the machine for cleaning. Concentrates from the first four cells go to the *Lead Thickener L* and thence to *Rotary Filter N* in which they are dewatered.

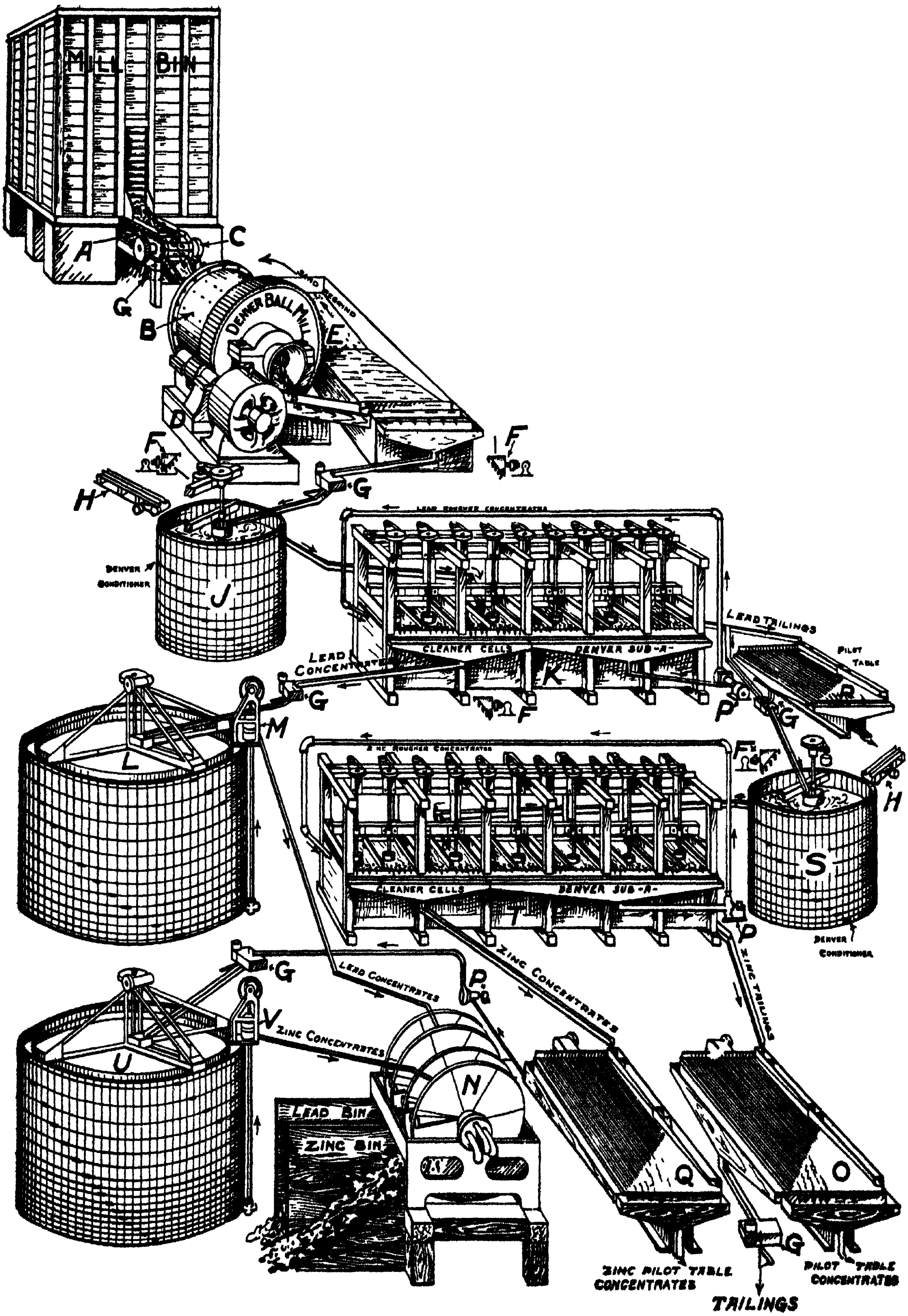
The tailings from the lead machine, containing the zinc, pass to *Conditioning Tank S* where are added the reagents required for the flotation of the zinc. A *Pilot Table R* is shown in the flow sheet which provides visual control of the efficiency of the lead float.

From *Conditioning Tank S* the pulp for zinc flotation is fed to the fourth cell of another ten-cell machine, *T*. Concentrates from the first four cells are clean zinc concentrates and are discharged to the *Zinc Thickener U* and thence to the *Rotary Filter N* for dewatering. The rough concentrates from the last six cells are delivered to the head of the machine for cleaning in the first four cells. *Pilot Tables Q* and *O* are for visual control of the operation of the zinc machines.

Flotation Machines.

The flotation machine itself may belong to one of two important types, pneumatic or mechanical, the former employing air not alone as the froth producer but also to keep the pulp in suspension, the latter relying upon mechanical agitation by means of a motor-driven propeller, rotor or the like. The pneumatic machines may be further divided into machines which admit the air through a diaphragm and free air machines. Examples of the former are the old style Callow machine and the more modern MacIntosh machine. The porous diaphragms may be either canvas or perforated rubber. The free air machines, such as the Forrester or Hunt, do not use diaphragms, the air being admitted through a series of open-end pipes or slits.

There are also a number of modifications of the mechanical machines, Minerals Separation and Fahrenwald machines with vertical propellers, *K* and *K* machines with a horizontal rotor. Auxiliary air beyond the amount


MILL BIN
A
C
G
B
DENVER BALL MILL
E
D
F
F
G
H
DENVER CONDITIONER
J
LEAD ROUGHER CONCENTRATES
CLEANER CELLS
DENVER SUB-A-
K
LEAD TAILINGS
PILOT TABLE
R
LEAD CONCENTRATES
G
F
P
G
L
M
ZINC ROUGHER CONCENTRATES
F
H
S
CLEANER CELLS
DENVER SUB-A-
T
P
DENVER CONDITIONER
G
LEAD CONCENTRATES
P
ZINC CONCENTRATES
ZINC TAILINGS
U
V
ZINC CONCENTRATES
N
LEAD BIN
ZINC BIN
Q
O
G
ZINC PILOT TABLE CONCENTRATES
PILOT TABLE CONCENTRATES
TAILINGS

sucked in by the propeller may also be introduced, such machines being designated "sub-aerated."

Examples of various types of flotation machines are given in the series of drawings shown below taken from the catalog of the Denver Equipment Company. The Denver Sub-A Machine described in Figure 8 has proven particularly successful in the handling of very coarsely ground minerals.

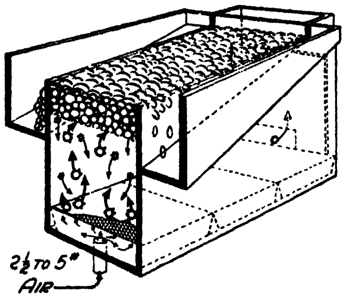


FIG. 1.

Long, trough-like pneumatic machine with sloping, flat, porous, canvas bottom. Level of entire cell controlled by weir gate at discharge end. Air added at bottom or top at $2\frac{1}{2}$ to 5 pounds pressure. Concentrates squeezed or pushed over sides of machine into launder.

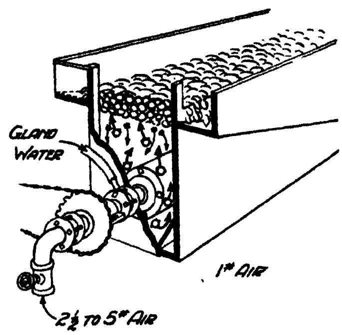


FIG. 2.

Long, trough-like pneumatic machine with air introduced through a rotating drum covered with a porous blanket. Rotating hollow shaft projects through ends of machine with stuffing box and gland water connection for seal; also has stuffing box connection for air pipe. Air introduced at $2\frac{1}{2}$ to 5 pounds pressure. Concentrates squeezed or pushed over sides of machine into launder.

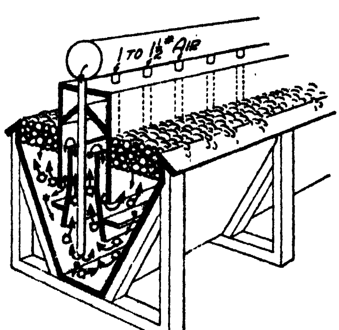


FIG. 3.

Long, trough-like pneumatic machine with air introduced in center, having air lift action through a row of free pipe openings. Air introduced at 1 to $1\frac{1}{2}$ pounds pressure. Concentrates squeezed or pushed over sides of machine into launder.

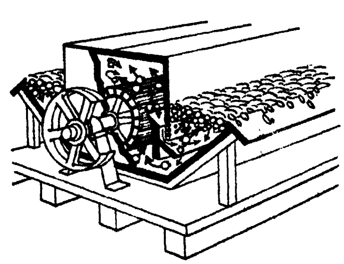


FIG. 4.

Long agitating chamber in which perforated drum rotates and mixes the pulp and the air. Rubber riffles on drum slats to take wear. A long, trough spitzkasten on front and also, if desired, on back of machine. Rotating drum has pulp ejector at each end to keep pulp from shaft openings at end of machine, while operating.

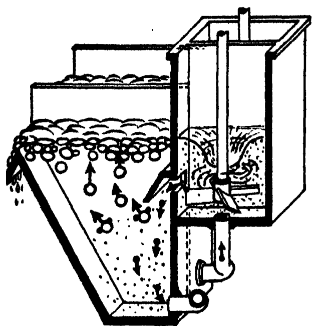


FIG. 5.

Machine consists of series of cells. Each cell has agitation chamber in rear and separation of froth and gangue takes place in spitzkasten. Pulp is conveyed from spitzkasten into adjacent agitating chamber by suction. Froth is removed by paddle shaft.

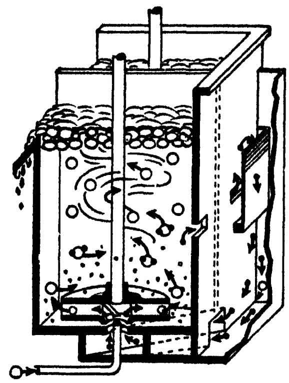


FIG. 6.

Machine consists of series of cells, each cell being a unitary agitating and separating chamber. Pulp is sucked into cell through narrow opening at bottom of cell up into closed impeller. Air under pressure is introduced into impeller with pulp. Impeller rotates in and at the bottom of chamber in which agitation and froth separation occurs. Froth is removed by paddle shaft.

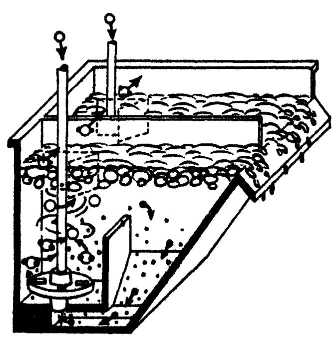


FIG. 7.

Aeration in agitating chamber secured by rotating impeller sucking pulp through narrow passage up into rotating impeller and drawing air through hollow rotating shaft. Impeller rotates in bottom of each agitating chamber, all of which are connected in one common level. Separation occurs in spitzkasten. Froth is removed by paddle shaft.

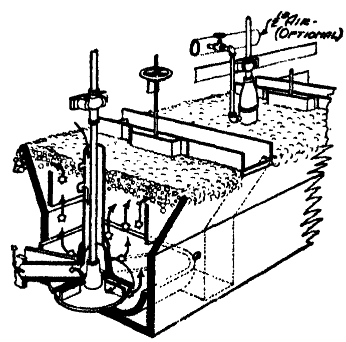


FIG. 8.

Denver "Sub-A" Flotation Machine consists of a series of cells each having a separate agitating and aerating zone with a spitzkasten for froth separation and removal. First cell shows feed by gravity, standpipe, stationary hood and impeller below hood. Usually sufficient air is sucked down standpipe by impeller below hood. Second cell shows how air at a very low pressure can be added. Circulation from cell to cell is entirely by gravity on pulp feed and middling returns. Concentrates are raised in direct line, with no conflicting currents, to quiet spitzkasten zone and removed by paddle.

Cost of Flotation.

Metallurgical operations must be conducted at low cost, because the per ton value of the ore treated is usually small. The flotation process is a low cost method of concentration. Costs of treatment by flotation depend upon a variety of factors such as the grade of the ore treated, the size of the plant and the number of concentrates produced. The cost of treatment of an ore at the rate of 25 to 50 tons per day of twenty-four hours might vary between $1.50 and $2.50 per ton of ore treated. The cost of a mill of this size would be in the neighborhood of $30,000 to $45,000. If 500 tons of ore are to be treated per twenty-four hours the cost per ton would be between 40 cents and one dollar. The cost of the mill would be between $175,000 and $250,000.

Flotation Reagents.

From the point of view of the chemist, the reagents employed in flotation constitute one of the most interesting parts of the story. Refinements in reagents have made possible greater delicacy in the separations effected. The number of reagents used has steadily increased; new needs have arisen and new reagents and reagent combinations have been developed to meet these needs.

As originally practiced, the sole flotation reagent was the bubble-forming material, that is, the *frother*. Following this came reagents adapted to assist the ore particles to enter the bubble wall, called collectors or *promoters*. Then came *depressors, activators,* and the less common of the chemical accessories of flotation.

The function of these groups of reagents may be made clearer if I am permitted to use an illustration which I have employed elsewhere,[4] in which the flotation operation was likened to a balloon ascension. The mineral to be floated is the aeronaut, the frothers are visualized as the material of which the balloon is made, the promoters are the rigging which binds the object to be floated to the balloon, and the depressors are the sand bags used by the balloonist to control his ascent.

Frothers.—Although a number of organic materials are available as frothers, only two are used to any considerable extent in practice. The most popular is pine oil, which is particularly indicated in the treatment of copper ores. Second in importance is cresylic acid which is generally selected for zinc-lead differential work. Besides these two there are several special oils used locally where available at low cost, such as camphor oil in Japan and eucalyptus oil in Australia.

In order to modify the texture of the bubbles, oils which are themselves non-frothing or only slightly frothing may be used in conjunction with the common frothing agents listed above. Examples are certain tar oils, which, in addition to small amounts of frothing constituents, contain heavy oils as well. These heavier oils act as froth stabilizers.

Certain of the promoters also possess frothing properties. Examples are the liquid Aerofloats made from cresylic acid, which are discussed in the section on promoters. In some cases no additional frother is required when these reagents are used. In other cases their frothing property is supplemented by the use of additional amounts of cresylic acid or of pine oil.

The amounts of frothing agent required per ton of ore depend upon a variety of factors. The consumption of pine oil per ton of ore treated probably varies between 0.05 and 0.20 lb. per ton. When cresylic acid is used,

larger amounts are usually required, the usage varying between 0.10 and 0.40 lb. of reagent per ton of ore treated.

In non-sulfide flotation, where oxides or carbonates are floated as such without the use of sulfidizing agents, the frothing agents usually employed are soaps or fatty acids. These reagents are also widely used in non-metallic flotation. Lack of selectivity is a characteristic of this type of froth and sharp separations are almost never possible when they are used.

During its early history flotation was practiced by the use of a single reagent which acted primarily as a frother. Some of the oils then used are now recognized to have contained small amounts of substances which possess the promoting property and doubtless owed some of their effectiveness to this fact. This early flotation practice permitted no selective work and may be called the *period of oil or bulk flotation.* With the introduction of chemical promoters a new era in flotation history was begun. This occurred in about 1920 with the introduction of alpha naphthylamine and thiocarbanilid. This modern period has been styled the period of *chemical flotation.*

Promoters.—The term promoter is used to designate a class of chemical compounds which, although they may not possess frothing properties, have the ability, when used in conjunction with a suitable frothing agent, greatly to increase the recovery of mineral. Occasionally the frothing and the promoter properties are combined in the same reagent, but the tendency at present is to separate them, since, by so doing it is possible to vary either property at will by varying the amount of frother or promoter used. Although there are a few operations where, on account of some special combination of circumstances, a chemical promoter is not used, these are very much the exception, and it is a safe assertion that 95 per cent of all of the flotation tonnage avails itself of the assistance of some member of the group.

The first promoters used in the industry were organic chemical compounds which were almost entirely insoluble in water, thiocarbanilide being one of the most effective. This fact misled many investigators who drew the erroneous conclusion that insolubility was a prerequisite. In practice these insoluble compounds were generally added in solution in other organic substances, the latter acting as frothing agents and also as dispersing agents for the promoters. Thus α-naphthylamine was dissolved in crude xylidines and thiocarbanilide was dissolved in *ortho*toluidine, the latter mixture being known in the trade as T-T mixture.

With the introduction of sodium or potassium ethyl xanthate into the flotation industry another important milestone was passed. The xanthates employed are all quite soluble in water. "Xanthate" is not only extraordinarily effective, but it is exceedingly cheap and it has set a very high standard for later competing reagents.

Following ethyl xanthate the xanthates derived from the higher aliphatic alcohols were introduced. These have proven even more effective than the xanthate derived from ethyl alcohol and may eventually displace it.

The last important additions to the promoter group of compounds are the alkyl and aryl dithiophosphates. These substances are produced by reaction between alcohols or phenols and phosphorus pentasulfide. They are sold under the trade name "Aerofloats." Aerofloat 15 and Aerofloat 25 are products derived from cresylic acid; sodium Aerofloat and Reagent 208 are salts of alkyl dithiophosphoric acids.

The xanthates and the dithiophosphates are very similar in their chemical makeup. The xanthates are alkyl dithiocarbonates, produced by reaction between the alcohols and carbon bisulfide. The dithiophosphates differ from

the xanthates only in the fact that they have phosphorus instead of carbon in the nucleus. Their formulas are given below where *R* represents an alcohol group and *X* a metal, such as sodium or potassium.

Xanthate	*Dithiophosphate*
$RO{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SX$	$\begin{matrix} RO \\ RO \end{matrix}{>}\overset{\overset{\displaystyle S}{\|}}{P}{-}SX$

The xanthate series is limited to the aliphatic series. In the case of the dithiophosphates either alcohols or phenols may be used.

In general, the xanthates are employed where a maximum amount of promoter activity is desired, and the dithiophosphates where greater selectivity is needed. There are, however, many exceptions to this generalization and in many cases the choice is dictated by personal preference. The xanthates are usually employed when flotation is conducted in highly alkaline solutions, for the reason that the dithiophosphates become too selective at high alkalinities and require hydrogen-ion concentrations near the neutral point to develop their maximum effectiveness.

Attention was called in an earlier paragraph to the greater effectiveness of the xanthates produced from higher alcohols. The same observation has been made in the case of the dithiophosphates, the potency of which increases with increasing molecular weight of the alcohol up to the alcohols with about five carbon atoms.

Some experimental data on the potency of some of these promoters will be of interest. The effectiveness of very small amounts of ordinary ethyl xanthate is shown in the first table. In a series of tests a copper ore was floated using pine oil as the frothing agent. In the first experiment no chemical promoter was used; in the subsequent experiments potassium ethyl xanthate was used in increasing amounts. The effect of increasing amounts of the promoter upon copper recovery is shown in the following table.

Promoter Pounds Potassium Ethyl Xanthate per Ton of Ore	Per Cent Copper Recovery
None	31.5
0.0125	77.3
0.0250	92.5
0.050	93.9

Thus, addition of only one-fortieth of a pound of promoter for each 2,000 pounds of ore trebles the recovery of copper. The ratio of concentration in this series of experiments was of the order of 4 into 1, hence the amount of mineral recovered by each pound of promoter was in the neighborhood of six tons.

In the next table we show the effect of increasing the molecular weight of the alcohol used in the production of a xanthate.

	Per Cent Copper Recovered			
Pounds of reagent per ton of ore.......	.01	.02	.04	.08
Ethyl xanthate	69.8	82.6	90.9	93.6
Isopropyl xanthate	76.4	89.8	94.9	96.1
Secondary butyl xanthate..............	82.4	91.3	95.3	96.8
Amyl xanthate (pentasol).............	86.9	93.5	95.0	96.0

Similar data have been obtained for the dithiophosphates. The rule as stated by Gaudin[5] is that "The activity of a collector from a homologous

series of compounds increases as the non-polar part of the reagent molecule increases."

It will be seen that we have very nearly reached perfection insofar as promoters for sulfide minerals are concerned. The limitations on recovery are now largely determined by such factors as fineness of grinding, degree of association of the minerals and the like, rather than by the reagent. There is, however, some room for improvement in that reagents more effective on oxidized ores may still be brought out. The higher xanthates and the higher dithiophosphates are both moderately effective on carbonate minerals, even without the use of sulfidizing agents. Their effectiveness is considerably increased by the use of sulfidizing agents. With the reagents now available it is possible to float with a fair degree of efficiency most of the naturally occurring carbonates. On the other hand, we are not able successfully to float the natural oxides and the silicates. Even when sulfidizing reagents are used the results are disappointing.

Activators.—This brings us to a discussion of methods of pretreatment or activation, including in this category sulfidizing agents, activating agents and pyrometallurgical pretreatments.

For the activation of oxidized minerals a soluble sulfide is generally used. Deposition of a film of metallic sulfide occurs on the surface of the oxidized mineral and the mineral so treated is then floated, using the ordinary reagents used for the flotation of natural sulfides. The success attending sulfidization varies with the mineral and with the method of application. Carbonates such as those of copper and lead respond fairly well to the treatment. Oxides and silicates respond poorly if at all. Usually the sulfidizing effect is transitory, presumably for the reason that the freshly precipitated sulfides are readily oxidized in the flotation cell. For this reason it is usually customary to add the sulfidizing agent to several cells of the flotation machine. A further disadvantage of sulfidization is that soluble sulfides act as depressants for certain minerals. Silver-bearing minerals are particularly subject to this effect and difficulties are frequently experienced from loss of silver due to this cause.

Sphalerite is almost always activated with copper sulfate before floating. Sphalerite itself is comparatively difficult to float but on agitation with soluble salts of copper its floatability is greatly improved. The mechanism of this action is presumably a double decomposition reaction resulting in the precipitation of copper sulfide on the surface of the sphalerite particles. Activation with copper sulfate takes place slowly and it is customary to allow a conditioning period, usually at slightly elevated temperatures, in order to complete it.

By "pyrometallurgical pretreatments" we refer to the treatment of oxidized minerals to reduce the metallic content to free metal. The "Segregation Process" now being studied for the treatment of oxidized copper minerals is a case in point. In this process the oxidized copper mineral is mixed with a small amount of carbon and salt and is heated in a rotary kiln. Reduction of the copper minerals to metallic copper occurs, and this is subsequently recovered by flotation.

This process depends upon the fact that free metals are recoverable by flotation almost as readily as are the sulfides, and by use of the same reagents. Tailings from mechanical concentration operations are now being treated by flotation in the Lake Superior district for the recovery of the small amounts of native copper which they contain. Native silver is being successfully floated in the cobalt district in Canada. The flotation of free gold is widely practiced. In some cases flotation is the only hydrometallurgical process em-

ployed, the flotation concentrate being shipped directly to the smelter. In other cases flotation is employed as an adjunct to cyanidation, a rough low-grade concentrate being produced by flotation which is subsequently cyanided, usually after regrinding.

Depressors.—Chemicals which render non-floatable or difficultly floatable, minerals which are otherwise readily floatable, are known as depressors. The term is usually restricted to chemical substances possessing no other function in the flotation circuit. Materials which are used primarily for other purposes are usually not classed as depressors even though they may possess the depressor property in some degree. An example is lime, which, although it acts as a depressor of flotation in the case of pyrite and free gold, is usually classed as a regulator rather than as a depressor.

Minerals whose flotation has been inhibited by use of a depressor may or may not subsequently be activated and floated. In the selective flotation of complex lead-zinc-iron ores the practice consists in first depressing the flotation of zinc and iron to permit the recovery of a high-grade lead concentrate and, following this, in activating the zinc without at the same time activating the iron so that the zinc can be recovered as free from iron as possible. After the lead and the zinc have been recovered in separate concentrates, the iron is sometimes recovered in a final flotation operation. In copper flotation the iron is depressed to permit recovery of a high-grade copper concentrate. Following this the iron may be recovered if it is desired to do so.

Although sodium sulfite was the first depressor used, it has been superseded in all but a very few operations by sodium or calcium cyanide. Very much smaller amounts of cyanide are required than of sulfite. Cyanide has set a high standard and has not been seriously threatened. For the depression of sphalerite it is usually used in conjunction with zinc sulfate. In the example given (see *supra* under the heading "Examples from Flotation Practice") of the separation of a complex lead-zinc ore 0.2 lb. of sodium cyanide and 0.70 lb. of zinc sulfate were used per ton of ore for the depression of the zinc and the iron minerals, and the lead mineral was recovered by use of about 0.1 lb. of ethyl xanthate. The zinc was then activated for flotation by addition of 0.9 lb. of crystal copper sulfate and the zinc was recovered by use of 0.15 lb. of Aerofloat 15. Following this about 0.2 lb. of ethyl xanthate was added and the iron concentrate was recovered.

Ores and minerals vary in their sensitivity to the action of cyanide. The flotation of lead is little affected even by large cyanide additions. Small amounts of cyanide will depress pyrite and permit the recovery of a high grade copper concentrate from a complex copper-iron ore. Larger amounts of cyanide, however, will depress the copper minerals as well. Of the more common copper minerals, chalcopyrite is less sensitive to cyanide additions than is chalcocite. In copper flotation the cyanide additions employed are of the order 0.01 to 0.03 lb. per ton of ore; with zinc-lead ores the requirement is higher, varying between 0.10 and 0.25 lb. per ton.

Regulators.—The term is used to include the acids or alkalis which are employed to regulate or control the hydrogen-ion concentration of the solutions in which flotation takes place. In a few cases no reagent of this type is employed, flotation being carried out in a so-called "natural circuit," that is in a solution having the hydrogen-ion concentration resulting from the combination of ore and water used. Such cases are the exception and it is usual practice to conduct flotation on the acid or the alkaline side of the neutral point.

Originally all flotation operations were carried out in acid circuits, but the

acid circuit has been gradually replaced by the alkaline circuit, so that at the present time there are only a very few operations in the world which use the former. In general, most minerals float more readily in acid than in alkaline circuits, and alkaline flotation would not be possible without chemical promoters. The disadvantages of acid flotation usually outweigh its advantages, among them being the lack of selectivity of acid floats and the serious problems of equipment upkeep which its use involves.

For acid flotation sulfuric acid is almost invariably used. As alkaline regulators only lime and soda ash are of importance. Lime is used wherever possible on account of its low cost. In copper flotation its use is almost universal. Lime is seldom used in zinc-lead flotation because of the fact that calcium compounds depress the flotation of lead. Soda ash is the usual regulator in zinc-lead flotation. Flotation operators now recognize the importance of accurate regulation of solution alkalinity; and pH control, either electrometrically or by use of indicators, is now common practice.

Alkalis perform a number of functions in the flotation operation. We have already referred to the fact that lime may sometimes act as a depressor. Alkalis also precipitate certain soluble salts from solution, some of which are objectionable. One of the most important effects of alkalinity is on the promoter used. For each promoter there is a hydrogen-ion concentration at which it performs best. For this reason it is usual practice in ore testing to conduct experiments at increasing alkalinities in order to determine the optimum for ore and promoter. The amounts of lime or soda ash required for best results vary with the ore and with the water used. Amounts as low as one pound per ton of ore and as high as ten pounds are not uncommon.

Miscellaneous reagents.—There are a few materials used in modern flotation which are not properly classified in any of the above groups. Examples are sodium silicate, glue, gelatin and the like, which are frequently used as gangue deflocculators. In general, flocculated particles tend to enter a bubble film, while deflocculated particles fail to do so. Promoters can be shown to flocculate sulfide minerals. Sodium silicate, on the other hand, usually functions as a deflocculator for siliceous slimes, keeping these materials out of the bubble so that a concentrate low in silica can be obtained.

THEORY OF FLOTATION.

Although the present discussion relates to the practice of flotation rather than to its theory, the latter cannot be altogether overlooked. We have defined flotation as a process for the separation of the constituents of a complex ore mixture which depends upon the fact that certain constituents, notably the sulfides, attach themselves to oily bubbles while others fail to do so or do so only with difficulty. Floatable minerals are therefore minerals more readily wetted by oils than by water, that is, hydrophobe minerals; and non-floatable minerals are those which are more readily wetted by water than by oil, in other words, hydrophile.

Frothing agents are polar non-polar substances, that is, chemical substances intermediate in their properties between such characteristically polar substances as caustic soda on the one hand and such characteristically non-polar substances as benzol on the other. When dissolved in water these substances lower the surface tension of water. At the air-water interfaces, they orient themselves so that the polar portions of the molecule face toward the water and the non-polar portions face the air. The surfaces of a bubble produced in a solution of a frothing agent may be considered similar to the surface of a drop of oil;

they are consequently capable of wetting the hydrophobe minerals and of repelling the hydrophile minerals.

Minerals normally hydrophobe, which have not been altered superficially by oxidation or ion adsorption, are capable of flotation without the assistance of chemical promoters. In practice, however, such unaltered surfaces are seldom encountered. Minerals with altered surfaces may be styled macro-ions, that is they are relatively large aggregates carrying electrical charges depending in amount upon the extent to which the oxidation or ion adsorption has taken place. By virtue of these electrical charges the mineral particles are rendered more or less polar and have, therefore, less tendency to leave the water and to attach themselves to the oily envelope of the bubble.

These macro-ions or charged mineral particles are capable of reacting with substances in solution. Their floatability is thereby increased or decreased, depending upon whether the resulting compound is less or more polar than the original macro-ion. By reaction with a promoter, a xanthate or a dithiophosphate as the case may be, the previously polar portions of the mineral surface are rendered non-polar, and the mineral is thus rendered floatable. By reaction with a cyanide a complex ion is formed which is still more polar than the original macro-ion; as a result the mineral particle resists all efforts of the oily coating of the bubble to wet it.

Considering specifically the differential separation of a lead-zinc-iron mineral, we suggest the following as the function of the various reagents. After preparation of the ore pulp for flotation by the usual grinding and classification, zinc sulfate and sodium cyanide are added to cause depression of the zinc and the iron minerals. The assumed mechanism is that zinc ions are adsorbed by the sphalerite particles, thus rendering them polar, and, consequently, less floatable than the original mineral particles. The macro-ions thus formed react further with cyanide ion to produce complex macro-ions, which are still more polar and consequently still less floatable than the original macro-ions. Since lead does not form complex cyanogen compounds, the lead minerals do not form complex macro-ions with cyanide; and as a consequence the floatability of the lead minerals is not reduced by the cyanide.

The mechanism of the depression of the iron minerals is similar to that of the depression of the zinc. Pyrite oxidizes very readily and the mineral particles become macro-ions either by virtue of the oxidation itself or by adsorption of iron ions from the solution. The macro-ions thus formed react with the cyanide to form the strongly polar ferrocyanogen macro-ions and the mineral particles, as a result of this polarity, will not enter the bubble wall. This explanation is supported by the fact that pyrites which has been completely freed from soluble iron salts by thorough washing, is not readily depressed by cyanide additions.

The assumed reactions may be represented by the following equations, where [ZnS] and [FeS_2] represent the sulfide particles before oxidation or ion adsorption has taken place.

$$[ZnS] + Zn^{++} \rightleftarrows [ZnS]\,Zn^{++}$$

$$[FeS_2] + Fe^{++} \rightleftarrows [FeS_2]\,Fe^{++}$$

$$[ZnS]\,Zn^{++} + 4CN^- \longrightarrow [ZnS]\,Zn(CN)_4^{--}$$

$$[FeS_2]\,Fe^{++} + 6CN^- \longrightarrow [FeS_2]\,Fe(CN)_6^{----}$$

Having rendered the zinc and the iron minerals non-floatable, a promoter is now added. Those lead particles which had become polar macro-ions either through oxidation or ion adsorption, react with the anions of the promoter to form a non-polar macro-molecule as shown by the equation

$$\underset{\text{(Polar)}}{[PbS]\,Pb^{++}} + 2RS^{-} \longrightarrow \underset{\text{(Non-polar)}}{[PbS]\,Pb(RS)_2}$$

where RS^- represents the promoter ion, xanthate, dithiophosphate, etc.

After the removal of the lead it is necessary to activate the zinc for flotation, and this is done by the addition of copper sulfate. Several possible reactions may be written, of which the following is one:

$$[ZnS]\,Zn(CN)_4^{--} + 2\,Cu \longrightarrow [ZnS]\,Zn^{++} + 2\,Cu(CN)_2$$

In other words the cyanide component is fixed by the copper as cupric cyanide (presumably later decomposing to cuprous cyanide), leaving the original zinc macro-ion, which then reacts with the anion of the promoter to form a non-polar macro molecule in exactly the same way as the lead macro molecule was formed.

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Chemical Warfare

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At best, war is a brutal and unethical procedure, the only excuse for it being necessity, the tyrant's plea. The hope of the future is that all mankind may become so enlightened that the admirable qualities of courage, faithfulness, and sacrifice shown by men in war may be sublimated so as to win the less spectacular but more important battles against pain, unhappiness and disease. Granting that all warfare is by its very nature cruel, it is no more wicked to asphyxiate people than it is to tear them to pieces with steel or explosives. It was the newness, effectiveness, and lack of adequate chance for escape or defense, that made chemical warfare seem so terrifying.

The shock of the successful and extensive use of "chemicals" in the recent World War led many to the view that chemical warfare is cruel and inhuman. Since bullets, and other missiles are propelled by explosive chemicals ("smokeless powder") and shells are fragmented by explosive chemicals (e.g. picric acid or "lyddite," trinitrotoluol or T.N.T.), and since these or substitute explosive chemicals are used in bombs, mines, torpedoes and grenades, it is at once evident that even before the Great War, warfare was based on chemicals. When to this we add the service of chemists in the preparation of metals, foods, medicines, and supplies of all kinds, it is evident that modern warfare could not exist without chemistry.

Chemical Warfare Among Animals.

A naturalist described the following combat: A large wasp was seen hovering above a huge spider, which kept circling, striving to keep facing its foe. The swoop of the wasp and the lunge of the spider were too rapid to follow—but the spider lay instantly paralyzed by the chemical injection of the wasp, and the wasp, disembowelled by the hooked mandibles of the spider, was in its death struggle. Was the "chemical" injection of the wasp more cruel than the slashing stab of the spider?

The "bombardier beetle" (Order, *Carabidae;* genus, *Brachinus*) ejects a fluid which volatilizes explosively on contact with air, giving a distinct report and a puff of smoke. This performance may be repeated several times in quick succession, and the vapor is acid and corrosive. Westwood reports that on seizing individuals of a large South American variety, they "immediately began to play off their artillery, burning and staining the flesh to such a degree that only a few specimens could be captured with the naked hand, leaving a mark which remained for a considerable time." P. W. Fattig [see *Science,* **70**, 193 (1929)] reports that a Brachinus (*Dicaelus*) captured in Georgia and dropped into a cyanide bottle, was completely hidden in the dense smoke evolved from the strong discharge of gas it emitted. When the bottle was opened, the smoke escaped over a foot from the opening.

Leaving the unnumbered species of insects that sting, bite, gnaw and tear,

* The writer acknowledges, with thanks, considerable assistance in the preparation of this paper.

we might mention the curious case of the termites driven by the fierce competition of insect life in Africa to live in trees. Of these, Julian Huxley says: *

> "None of the tree-termite nests that I examined had any of the typical soldiers, huge-jawed and massive-headed, which defend the ordinary ground nests. In their place there swarm out as defenders the most fantastic creatures, their heads swollen and drawn out like the neck of a phial. In point of fact, their heads *are* phials. They are filled with glands which secrete a horribly adhesive material, and their method of fighting is to squeeze some of this out at the hole at the tip of the phial-spout, thoroughly gumming up their enemies."

Going to the sea,† we find the Portuguese man-of-war whose terrible stinging power is characteristic of most of the Colenterates. The cuttle-fish (an arthropod), when attacked, can squirt out a cloud of sepia to confound its enemies. In fresh water, the electrical eel or the gymnotus may easily floor a man.

Among mammals, the skunk is a familiar though perhaps unwelcome acquaintance. He moves with dignity and the unhurried assurance begot of confidence, and with a chemical armament speedily converts his enemies to meek pacificism.

Historical Aspects.

The history of chemical warfare goes back to remote antiquity. The Chinese are credited with the original discovery of gunpowder, and Chinese and Malay pirates for time out of mind have used stink-pots. "Greek Fire" is said by some to consist of pitch, sulfur, tow, frankincense and pine sawdust. Others state that it contained sulfur, naphtha, wax, oil of balm, and quicklime. Possibly an oxygen-supplying substance was a secret ingredient. In 429 B. C. when the Spartans besieged Plataea, they lighted great pots of pitch, sulfur and charcoal near the walls, so that the irritating gases would blow over to the defenders of the city. Lime dust was largely used in medieval warfare to choke and blind, and the late Dr. Beebe, Librarian at Edgewood Arsenal, collected data on biological attacks; e.g. earthen pots filled with poisonous reptiles were thrown on the decks of enemy ships. Stink bombs were known and used in the Middle Ages and an old Austrian chemist, Vlit Wulff von Sensftenberg, in 1573, said of them: "It is a terrible thing. Christians should not use it against Christians but they may use it against the Turks and other unbelievers to harm them." In 1632, Gustavus Adolphus of Sweden crossed the Lech River, near Augsburg, under cover of a smoke cloud produced by burning straw, and overwhelmed his unsuspecting enemy. In 1699, using a similar screen, his successor Charles XII crossed the Dvina River and defeated the Saxons.

Prof. James F. W. Johnston in his book "The Chemistry of Common Life" (2nd ed. 1879) in speaking of "The Smells We Dislike," said:

> "Imitating the natural habit of the skunk in this respect, we might far surpass it in the intensity and offensiveness of our artificial stinks. Squirted from the walls of a besieged city, projected into the interior of a fortified building or diffused through the hold of a ship of war, the Greek fire would be nothing to them; and as for the stink-pots of the Chinese, they must be mere bagatelles to the stenches we can prepare."

And later, in referring to cacodyl cyanide,‡ he said:

> "These kakodyls and their cyanides might certainly be employed, could they be prepared and transported safely in sufficient quantities, still more efficiently in warlike opera-

* Harper's Magazine, October, 1930.
† The sword-fish, the saw-fish, the sting-ray, the doctor-fish are a few among the many denizens of the sea furnished with special means of offense.
‡ E. K. Fradkin (*see* Bibliography) quotes a recent claim that this is a *new* "poison gas"!

tions; but how far the use of vulgar poisons in honourable warfare is consistent with the refinements of modern civilization, is open to much doubt. There may not be much real difference between causing death by a bullet, and by the fumes of deadly poison; and yet, to condemn a man 'to die like a dog,' does array death to him in more fearful colours."

Johnston also referred to the development of charcoal respirator, which was treated at length by Dr. J. Stenhouse and is described in a paper by Dr. Wilson in 1854, reported in the *Transactions of the Royal Scottish Society Arts,* **4,** Appendix O, p. 19. The report states:

"The longing for a short and decisive war has led to the invention of 'a suffocating bomb shell,' which on bursting, spreads far and wide an irrespirable or poisonous vapour; one of the liquids proposed for the shell is the strongest ammonia, and against this it is believed that the charcoal respirator may defend our soldiers. As likely to serve this end, it is at present before the Board of Ordinance.

"Dr. Wilson stated, in conclusion, that Dr. Stenhouse had no interest but a scientific one in the success of the respirators. He had declined to patent them, and desired only to apply his remarkable discoveries to the abatement of disease and death.

"In 1855 Admiral Dundonald having observed the deadly character of the fumes evolved by obtaining sulphur in Sicily, outlined an attack on the Russians at Sebastopol, estimating that he would need four or five hundred tons of sulphur and two thousand tons of coke to burn and vaporize it.

"Besides these many materials it would be necessary to have, say, as much bituminous coal and a couple of thousand barrels of gas or other tar, for the purpose of masking the fortifications to be attacked or others that flank the assailing positions. A quantity of dry fire wood, chips, shavings, straw, hay and other such combustible materials would also be requisite to quickly kindle the fires, which ought to be kept in readiness for the first favourable and steady breeze."

B. W. Richardson [*Popular Science Review,* **3,** 176 (1864)], in an article on "Greek Fire," * said:

"I feel it a duty to state openly and boldly, that if science were to be allowed her full swing, if society would really allow that 'all is fair in war,' war might be banished at once from the earth as a game which neither subject nor king dare play at. Globes that could distribute liquid fire could distribute also lethal agents, within the breath of which no man, however puissant could stand and live. From the summit of Primrose Hill, a few hundred engineers, properly prepared, could render Regent's Park, in an incredibly short space of time, utterly uninhabitable; or could make an army of men, that should even fill that space, fall with their arms in their hands, prostrate and helpless as the host of Sennacherib.

"The question is, shall these things be? I do not see that humanity should revolt, for would it not be better to destroy a host in Regent's Park by making the men fall as in a mystical sleep, than to let down on them another host to break their bones, tear their limbs asunder and gouge out their entrails with three-cornered pikes; leaving a vast majority undead, and writhing for hours in torments of the damned? I conceive, for one, that science would be blessed in spreading her wings on the blast, and breathing into the face of a desperate horde of men prolonged sleep—for it need not necessarily be a death—which they could not grapple with, and which would yield them up with their implements of murder to an enemy that in the immensity of its power could afford to be merciful as Heaven. . . .

"To conclude. War has, at this moment, reached, in its details, such an extravagance of horror and cruelty, that it can not be made worse by any art, and can only be made more merciful by being terribly energetic. Who that had to die from a blow would not rather place his head under Nasmyth's † hammer, than submit it to a drummer-boy armed with a ferrule?"

In the year 1899 a peace conference was held at The Hague and attending this conference were representatives from every country in the world. At this conference, the subject of using poison gas in war was introduced and, after thorough discussion, it was finally decided that the use of gas-filled shell

* During the American Civil War some Confederates, who managed to run the blockade, tried to set fire to New York City by pouring solutions of phosphorus in carbon disulfide in concealed places, e.g., in a clothes closet of the old Astor House. The fumes and lack of air rendered the attempt nugatory, and years after one of the plotters feelingly remarked to the Editor: "Greek fire is a lost art!"

† James Nasmyth (1808-1890), a Scotchman, invented the steam hammer.

was inhumane and against the laws of civilization. All of the representatives of the conference but one agreed to renounce forever that method of warfare. The member opposing this action was none other than the U. S. representative, Admiral Mahan, who held that the use of asphyxiating gases was no worse than the use of weapons then permitted. He voiced his objections in the following terms:

"1. The objection that a machine of war is barbarous has always been raised against new weapons which were nevertheless finally adopted. In the Middle Ages it was fire-arms which were denounced as cruel. Later, shells, and more recently, torpedoes have been denounced. It seems to me that it cannot be proved that shells with asphyxiating gases are inhumane or unnecessarily cruel machines of war, and that they cannot produce decisive results.

"2. I represent a people that is animated by a lively desire to make warfare more humane, but which may nevertheless find itself forced to wage war; therefore, it is a question of not depriving itself through hastily adopted resolutions of means of which it could later avail itself with good results."

Twenty-five years later the world was plunged into the greatest war in history. This war had progressed only a few months when it was realized that the mechanical method of conducting war, which had attained its highest degree of perfection, was making no headway, and the system of war was reinforced by more effective and scientific methods. One reason for this was the underground or dug-in method of warfare which was not anticipated.

The introduction of gas was not only responsible for the bringing of the war to an earlier close, but it has also served the purpose of introducing into modern warfare a scientific weapon which, if successfully used, would prove to be most effective, most inexpensive and by far the most humane of any of our war machinery.* If disastrous results are to be avoided from its use in the hands of the enemy, education in gas matters, training with gas appliances, strict discipline and facilities for administering relief to its casualties, must be provided.

During the World War chemical warfare was not used to any great extent in the navies participating. Likewise, none of the contending forces of the aviation corps used chemical bombs against each other. While it has been stated that gas was used in the Battle of Jutland, an official report does not bear out this statement. It is true there were many gas casualties, but these appear to have been caused by carbon monoxide gas resulting from the explosion on shipboard of projectiles and from flames and burning cordite.

There are two outstanding cases, however, in which gas was used in naval action during the War. During the attack on H.M.S. Vindictive on the Mole at Zeebrugge, April 22-23, 1918, the crew was subjected to a gas, the nature of which is not known, but it was strong enough to penetrate every part of the ship, especially between decks. Here gas masks came into good play. M. Schwarte, in "Die Technik in Weltkriege," 1920, page 303, states that in the Battle of Skagerrack the fleet used with excellent results box respirators to protect against the effects of nitrous gases which were prevalent.

* The comparative percentage ratios of deaths to casualties in the Great War were:

	Gas	Other Weapons
American Army	2	25.7
British Army	3.3	36.6
French Army	2.9	43
German Army	3.1	36

In the Civil War the deaths approximated 29 per cent of the casualties; in the Franco-Prussian War, 29 per cent; in the Russo-Japanese War, 35 per cent.

The after-effects of gas casualties are generally much less severe or lasting than those from shot and shell. The rigors of war must also be considered as contributory, if not primary, causes of many after-effects in gas cases.

Since all nations have been working assiduously on gas offense and defense, what has happened in the past is no criterion for the future, where new compounds and higher concentrations may be employed. Whoever begins a war today will face the execration of mankind.

Later Developments—Action and Use of "Gas."

At the beginning of gas warfare, but four or five different kinds of chemicals were used, but as war progressed this number was greatly increased until it reached hundreds. Later, however, the number was rapidly reduced until at the present time the number of effective war chemicals can be counted on the fingers of both hands—mainly materials which can be made cheaply and in quantity.

The physical states of these chemicals vary; some being true gases, like chlorine or phosgene; others liquids, of which mustard ($\beta\beta'$ dichlorodiethylsulfide, $(C_2H_4Cl)_2S$) and Lewisite (β-chlorvinyldichlorarsine, $ClCH = CHAsCl_2$) are good examples, and still others are solids, like those comprising the lachrymators, e.g. chloroacetophenone ($C_6H_5COH_2Cl$) and brombenzylcyanide ($C_6H_5CHBrCN$). It is the gases or vapors from these that are to be feared; in referring to any of them, whether they are true gases, liquids or solids, the term "chemicals" is used. A further study of these chemicals reveals the fact that some volatilize slowly, while others are just the reverse. The slow-volatilization gases are spoken of as "persistent gases"; the others "non-persistent."

The action of war chemicals on the human organism is like that of any other destructive agent and a parallel may readily be constructed between the action of gas-filled and explosive projectiles. The ordinary shell kills when it reaches a vital organ, such as the heart, the brain or the large blood vessels, and wounds when it affects a minor organ, such as the bones, the limbs, etc. Similarly, gas kills by the annihilation of some primary function. Hydrocyanic acid gas, for example, paralyzes the nervous system, carbon monoxide poisons the blood, and the action of such gases as chlorine and phosgene in high concentrations destroys lung activities. A gas may be said to wound when it destroys either permanently or temporarily any function which is indispensable during combat. The lachrymators which temporarily impair the sight and the substances which interfere with respiration produce casualties as serious to efficiency as those caused by rifle bullets or shell splinters. Finally, both ordinary traumatism and the result of gas action are accompanied by the danger of infection. From the military point of view, therefore, gas casualties do not differ from the temporary or permanent disabilities produced by other means.

The chemical agent is a universal weapon, for it is adaptable to all arms. It is a necessary and efficient auxiliary in every operation. Its use must be considered essential in every tactical situation.

Let us examine then the status of this weapon today beginning with use of chemicals in *gas clouds,* the form in which gas was first introduced. Space does not permit a detailed description of each device.

The first attacks were made by releasing chlorine contained under pressure from steel cylinders which weighed for the Allies approximately 180 pounds when filled. In order to carry out a cloud attack of any size a vast amount of labor and preparation was required. To install 150 cylinders, troops had to carry up nearly fourteen tons of material. For this reason cylinders were relegated to a position of minor importance during the last half of the war, although they were effectively employed by the British in the latter part of 1918. In these instances the disadvantages were overcome by massing cylinders on flat cars or trucks, moving the trains or trucks rapidly forward as far as possible, and releasing the gas by electricity.

The value of a cloud gas lies in the fact that high concentrations in vapor form can be made to cover any desired front with little or no warning. In a steady favorable wind, a cloud may be launched covering several miles in such high concentration as to penetrate inferior, weakened or defective masks even after traveling two to three miles from the point of release. Using such a cloud at night, the surprise effect inevitably results in casualties, since many men will be caught unmasked.

The *Livens projector* is a crude form of mortar designed to throw large quantities of chemical agent in high concentration on moderately distant targets. It amounts to forming a gas cloud at the target. It consists of a steel barrel dug into the earth at a proper angle, a propelling charge, on top of which is laid a shell, and the whole connected in batteries and fired electrically.

Projectors were continuously and successfully employed by all belligerents during the last year of the World War. The weapon has a maximum range of about 1,600 yards. It permits the rapid delivery of chemicals on a target in higher concentration and in a shorter space of time than is obtainable by any other munition that is projected.

In order to lay down large quantities of gas and incendiary easily and without special preparation, the British designed the 4-inch *Stokes Mortar.* It was the largest caliber weapon that could be fired rapidly and yet be mobile. It is adaptable for delivering gas, smoke, incendiary and high explosive. Its range is 200 to 1,200 yards. Rapidity of fire more than compensates for inaccuracies in laying or operation under field conditions. The mortar can fire up to 20 rounds per minute for one to two minutes.

The Stokes mortar has general application. It is especially effective against small definite targets, for casualty effect or for the production of blinding smoke. It is also advantageously used for screening movements within our own lines.

During recent years, the Chemical Warfare Service has developed the 4.2-inch Chemical mortar. The difference in caliber results from the rifling of the old 4-inch mortar. This weapon has a range of 2,400 yards, double that of the old mortar, has increased mobility, and will deliver a greater amount of gas. Being rifled it has much greater accuracy.

Chemical artillery shell are a permanent factor in modern warfare. Tear gas shell made their appearance as early as 1915. These were followed the next year by lethal shell containing a variety of agents, by smoke and irritant smoke shell, and incendiaries. When mustard gas was introduced in the summer of 1917, its unique tactical value and demonstrated efficiency as a casualty producer * so far surpassed all other chemical agents that it brought about a stabilization of chemical shell design, a reduction in the number of agents used, and an increase in the proportion of chemical shell to all other shell used. About forty different fillings covering a wide range of power and effect were employed. Germany had adapted chemical agents for use in all caliber weapons above the 37 mm. gun. The requirements for gas and smoke shell had increased so greatly at the close of the War that their use was limited only by production.

Chemical shell, unlike high explosive, does not require complete fragmentation of the shell. The efficiency of the high explosive shell is measured largely by the violence with which the jagged fragments strike their objective. With chemical shell, however, fragmentation is incidental since ordinarily the shell need contain no more explosive than is necessary to split it open, crack the base, and adequately scatter the contents. With certain chemicals, however, the shell may be both a chemical and high explosive shell at one and the same time.

When a high-explosive shell bursts on the ground the effect is principally lateral, reaching the targets only within the radius of burst, and is entirely spent within a few seconds thereafter. A liquid chemical shell burst on the ground tends to carry its charge in the direction of travel. The agent is thrown in all directions by the force of the explosion, partly in liquid and partly in vapor form, and some liquid enters the ground. In the case of non-persistent agents, the liquid spattered on the ground is rapidly converted into a vaporous cloud, which immediately moves away from the point of burst under the influence of the speed and direction of the wind. Large numbers of chemical shell burst near together form many small clouds which merge into a single extensive cloud of very high initial concentration. Continuous fire will continue the generation of the cloud. In the case of persistent chemicals a large portion of the chemical spatters on the ground. That in the air acts as a non-persistent gas; but the evaporation of the chemical on the ground will continue to pour into the air a dilute cloud so long as there is any liquid remaining. This evaporation is hastened by heat, as from the sun's rays, is retarded by cold, and practically stopped by freezing. It is thus seen that chemical shell produce a continuity of action in point of time, not only on the immediate target, but over downwind areas; and that the effect may continue for hours, days, or even weeks, depending upon the agent used and the weather.

Colloid-chemical Aspects of Chemical Warfare.

These may be epitomized as follows:

(1) *Offense.*—Irritant or otherwise inimical smokes or mists, which may be formed by explosive fragmentation of the poisonous material, or result from

* Casualties from mustard gas are generally incapacitated for six weeks or more. As many as 1,000,000 mustard shells were used in one 10-day attack.

deposition of such material upon atmospheric nuclei * (e.g., dust, water droplets). The materials may be distributed by bombs, shells, smoke candles, portable sprayers, etc. Smokes may be used to screen attacks.

(2) *Defense.*—As new mask- or filter-passing materials developed, gas masks and filters were improved to provide defense. While true gases are, for the most part, readily provided for in the gas-mask canister, colloidal mists proved most troublesome. The possibility of causing relatively rapid coagulation of mists, smoke screens, etc., is well worthy of study. Smokes may also be employed defensively, e.g. to blind attackers or to cover retreat.

(3) *Signalling.*—Special organic dye materials vaporized, e.g. by smothered combustion of lactose and potassium chlorate, give off characteristically colored smokes. Satisfactory colors are the following: *Red,* "paratoner" (made by diazotization); *yellow,* chrysoidine + auramine; *blue,* indigo; *purple,* indulin (?); *green,* auramine + indigo. Such smokes are readily seen and understood by men scattered over wide areas, and even hidden in trenches or shell holes. They are readily produced by relatively unskilful men from readily carried apparatus.

"Thus smoke has already begun to complicate, and in the future will complicate still more, every phase of fighting. It will be used for deception, for concealment, for obscuring vision, for signalling, and to hide deadly gases. The signal rocket will be used to start battles, change fronts, order up reserves, and finally to stop fighting.

"The signal smoke by day will be displaced at night by brilliantly colored lights which will have the same meaning as similarly colored smokes during the day. Thus, literally, smoke in the future will be a cloud by day and a pillar of fire by night to guide the bewildered soldier on the field of battle with all its terrors and amidst the confusion, gas, smoke and dust that will never be absent while battles last." (*See* Fries and West, pp. 330-35.)

Fine dispersions of solid or liquid particles in air are termed *aerosols.* Their formation, degree of dispersion, particulate motion, stability, and behavior have been considered at length in the paper of Prof. Wm. E. Gibbs in Vol. I of this series, pp. 393-419.† Aerosols used in chemical warfare are termed *smokes,* and are divided into *screening, irritant* and *signal* smokes.

Smoke materials may be dispersed by mechanical, thermal, or chemical methods, or a combination of these. Thus *phosphorus,* scattered mechanically by explosion of a shell, takes fire, its oxidization yielding a cloud of phosphorus pentoxide, which by absorption of atmospheric moisture forms a lasting smoke of high obscuring power. Besides this, phosphorus has a great incendiary effect. Other smoke producers are *sulfur trioxide,* generally used in its sulfuric acid solution (*oleum*); *chlorsulfonic acid* ($HOSO_3$-Cl), largely used on the German side by being dropped onto quicklime; *tin, silicon* and *titanium tetrachlorides,* which are hydrolyzed by atmospheric moisture, with formation of a mixed cloud of the respective hydrates and hydrochloric acid; *ammonium chloride,* sometimes made by union of NH_3 and HCl gases, but often a constituent of other smokes.

One of the most important smoke materials used at the present time in the United States Army is the so-called "smoke candle." The American "B. M. Smoke Candle" (so called because it was largely developed by the Bureau of Mines at the American University Experiment Station) was a development of the French candle which contained the Berger mixture, named after the originator. The principal components of this mixture were finely divided metallic zinc 25 parts and carbon tetrachloride 50 parts.

* *See* paper by Carl Barus on "Atmospheric Nucleation," and also papers by W. E. Gibbs, A. Einstein, W. H. Martin, and René Audubert in Vol. I of this series.

† Many aerosols (fine dusts) are highly explosive and have wrecked factories and killed workers. *See* Gibbs' paper.

$$2Zn + CCl_4 = 2ZnCl_2 + C$$

As the above equation indicates, the products are zinc chloride and free carbon, both of which pass off in the smoke. Since the mixture of these materials would be too fluid and the zinc powder would settle out quickly, there were added 20 parts of zinc oxide and 5 parts of "kieselguhr." The last two materials did not enter into the reaction and did not form a part of the smoke, but were used merely as absorbents for the carbon tetrachloride and to keep the latter and the zinc uniformly mixed.

This mixture produced a gray smoke due to the presence of the free carbon which was considered objectionable on account of the fact that dark smokes do not have as great obscuring power as white smokes of the same density. But, in addition, the reaction also lacked vigor and the materials were not fully utilized.

Starting then with the original Berger mixture, the American investigators developed the "Standard B. M. Mixture," which has the following percentage composition: Zinc, 35.4; carbon tetrachloride, 41.6; sodium chlorate, 9.3; ammonium chloride, 5.4; magnesium carbonate, 8.3. The sodium chlorate ($NaClO_3$) oxidizes the free carbon generating considerable heat, and carbon dioxide, an inert gas which not only helps to carry the zinc chloride smoke out of the candle, but also, by diluting the smoke, helps to a certain extent to prevent the agglomeration of the smoke particles.

The ammonium chloride serves to control the rate of burning of the candle by keeping the temperature down, and to produce a large volume of gas in the mixture, due to its dissociation on heating. This also serves to carry the smoke out of the candle and to prevent agglomeration. Any NH_3 and HCl formed recombine and add to the smoke.

The magnesium carbonate is an absorbent for the carbon tetrachloride, and is easily decomposed on heating into carbon dioxide and magnesium oxide. Since the magnesium oxide is very light and finely divided, it is largely carried out of the candle, so that there is very little solid residue left behind. Thus the magnesium carbonate also serves to not only increase the volume of gases generated but also to add to the volume of the smoke.

The Bureau of Mines also found that hexachlorethane (C_2Cl_6) can be satisfactorily substituted for carbon tetrachloride in the B. M. mixture. The chief advantage of this compound is the fact that it is a solid at ordinary temperatures (its melting point being 186° C.). It was found, also, that a very good smoke, though gray in color, can be obtained from a mixture of zinc and hexachlorethane alone, in theoretical proportions (about 22.5 parts of zinc to 27.5 of hexachlorethane). The mixture in use at present and called the Hexachlorethane or H. C. Mixture is essentially zinc, zinc oxide and hexachlorethane. The smoke produced is harmless and can be breathed without discomfort. The smoke hangs well and is persistent. The total obscuring power value is highest on a cold damp day and lowest on a warm dry day, varying from 850 to 1400.

The British "S" type candle contained a mixture of nitre (potassium nitrate, KNO_3), coal dust, sulfur, borax and hard pitch. The nitre was supposed to oxidize the sulfur and coal dust and the heat so developed distilled off the pitch. It is more than probable, however, that a part of the pitch was also oxidized, and that a part of the sulfur was likewise distilled off. The smoke produced by this mixture is light brown in color, but has low density, and hence low obscuring power. The mixture, furthermore, does not burn evenly and leaves a large amount of residue.

The Germans used a candle which contained a mixture of potassium nitrate (KNO_3), sulfur and realgar (a natural sulfide of arsenic, As_2S_2). This mixture, on ignition, gives off a heavy yellowish smoke.

The naval smoke screen (black) is produced by the incomplete combustion of fuel oil, the oil being sprayed into the furnace under the ship's boilers with an insufficient supply of air and the smoke coming out of the funnels (smoke stacks). This smoke consists largely of free carbon, together with more or less tarry matter, and is essentially lamp black. The air service has also produced a black smoke screen by introducing lamp black into the exhaust pipe of the motor, to simulate a burning airplane.

Irritant Smokes.

After arsine proved a failure, chemists turned their attention to the organic compounds of arsenic with much better results. These compounds are very numerous, and many of them are toxic. They had also been previously studied quite extensively because many have valuable medicinal properties. A considerable number of these compounds were found to be useful in chemical warfare. The best known examples are Lewisite (β-chlorvinylchlorarsine), methyldichlorarsine, ethyldichlorarsine, diphenylchlorarsine, diphenylcyanarsine, and diphenylaminechlorarsine. The Chemical Warfare Service adopted only three of these compounds as standard chemical agents, namely, Lewisite, diphenylchlorarsine and diphenylaminechlorarsine. Lewisite does not resemble the other two in properties. Diphenylchlorarsine (D.A.) and diphenylaminechlorarsine (D.M.), however, resemble each other very closely.

These two compounds are placed in a separate class among chemical warfare agents and are known as Irritant Smokes because they do not produce their irritant effect by the formation of vapor, but by minute, finely divided solid particles, which are liberated in the air, thus forming a true smoke. This is due to the fact that they both have very high boiling points and consequently extremely low, almost negligible, vapor pressures. They produce their irritant effect by the entrance of the small solid particles into the lungs. These particles, being solids, cannot come into sufficiently intimate contact with the chemicals in the canister to be removed thereby, and the only means of protection, therefore, is mechanical filtration.

The finer the particles, the more lasting the smoke and the more difficult the problem of protection. A much higher concentration can be maintained with very fine particles, and hence the toxic effect is greatly enhanced. Very minute particles produce severe toxic effects, while larger ones produce merely excessive sneezing. When these compounds were first used, it was not known how to produce the very small particles and, hence, the compounds were called "Sternutators" or sneezing compounds. Some compounds are known whose effects are entirely limited to intense sneezing, but D.A. and D.M., when properly dispersed, have marked toxic properties. They are violent irritants to the nose and throat and in addition cause great distress. Nausea, vomiting and great prostration follow soon after breathing these smokes, with violent sneezing and coughing. Headache may be intense and last for several hours. An unprotected man may be sick for ten or twelve hours or more but these smokes seldom, if ever, kill in concentrations met in the field.

The Army Gas Mask.

The soldier fighting in clouds of chemical agents (gas) is confronted with the same hazards that coal miners, firemen and chemical plant operators have

to face and like these men, the soldier wears a gas mask in order to eliminate from the air breathed all irritating and toxic gases, dusts or vapors. The toxic gases and dusts encountered in industry are of the same general nature as the chemical agents of warfare; in fact, some of the chemical agents of warfare are industrial chemicals but the Army gas mask is *not* suitable for general industrial use nor are industrial masks suitable for the use of the Army. The reason for this is that the Army gas mask is designed for use in the open, for protection against relatively low concentrations of every conceivable chemical agent which may be effectively employed in warfare; whereas, each of the various types of industrial masks is designed for use in enclosed spaces where relatively high concentrations of a particular gas or group of gases may be encountered.

The Army gas mask is, however, similar both in appearance and operation to industrial masks. It consists of a rubber facepiece which is connected by a corrugated rubber hose tube to a tin can known as the canister. The facepiece fits snugly to the face so as to be gas-tight and is held in place by an elastic head harness. Incoming air enters the canister where it is purified and then passes through the hose tube to the facepiece, impinging on the eyepieces, so as to prevent fogging. A flutter valve extending below the chin of the facepiece provides an exit for exhaled breath. The eyepieces are made of non-shattering glass and in one type of facepiece there is a diaphragm which permits of conversation.

The protection afforded by the gas mask is provided by the canister. The canister is fitted with a filter whose function is to *filter out irritating or toxic smokes and dusts,* and is filled with chemicals which *adsorb or neutralize toxic gases or vapors.*

The chemical filling consists of activated charcoal and soda lime. The activated charcoal adsorbs organic vapors such as mustard gas, Lewisite, chlorpicrin, cyanogen chloride, alcohol, benzene and carbon bisulfide and to some extent, acid gases such as phosgene, chlorine, hydrocyanic acid and sulfur dioxide. These acid gases are eliminated more effectively, however, by the soda lime with which they combine chemically.

The nature of the adsorptive power of charcoal for gases and vapors is not definitely known. It is known, however, that it does not involve an absorption similar to the manner in which water is absorbed by a sponge, nor does it appear to involve chemical action although this theory has been advanced. It would seem that adsorption involves a force or attraction for gases and vapors similar to the attraction of a magnet for iron filings.

The procedure for producing highly adsorptive charcoals, known as activation, was developed during the War and cocoanut shells were found to be the best raw material. The process for converting cocoanut shells into activated charcoal consists in first reducing these shells to charcoal (crude char) by heating or burning in an atmosphere deficient in oxygen just as ordinary charcoal is produced. Subsequently the crude char is again heated in streams of air or steam so as to eliminate by distillation and oxidation all oils and tarry matter in the microscopic pores or channels which extend throughout the mass of the charcoal. It is in these microscopic pores that gases and vapors are condensed and tenaciously held.

There is, of course, a limit to the adsorptive capacity of activated charcoal and further the adsorptive activity decreases as the amount of gas adsorbed increases. Also, some gases are adsorbed more readily than others; as a general rule the more readily the liquid or liquefied gas vaporizes, the less readily is it adsorbed. There is thus very little adsorption of air or such

gases as hydrogen or carbon monoxide or illuminating gas by activated charcoal.

There are a number of toxic gases, such as carbon monoxide and ammonia, for which neither the charcoal nor the soda lime of the Army gas mask canister afford protection, although adequate protection against these gases could be provided if necessary. Silica gel, as a canister filling, affords protection against ammonia; and Hopcalite, a mixture of oxides of cobalt, copper, manganese and silver, affords protection against carbon monoxide.

Silica gel and Hopcalite are not employed in the Army gas mask, for the reason that ammonia and carbon monoxide cannot be effectively employed in warfare. They dissipate so rapidly in the open that the soldier is not apt to encounter dangerous concentrations even if attempts were made to use these gases as chemical warfare agents. Silica gel and Hopcalite are, however, very important components of the canister filling for certain industrial and Navy Submarine gas masks. Silica gel is the essential filling for gas mask canisters required by refrigeration plant operators who encounter dangerous concentrations of ammonia; and Hopcalite is employed in gas mask canisters used in coal mines, in fighting fires, and also in submarines where dangerous concentrations of carbon monoxide may be encountered.

Each of the various types or groups of toxic gases and vapors thus requires special chemicals for canister filling in order to provide protection. There is at the present time no toxic gas vapor or dust known for which a fair degree of protection cannot be provided. Canisters can be made up with fillings such that they will eliminate from the air breathed any one or all of these toxic gases or dusts. No canister, however, affords protection indefinitely. The life of the canister is dependent not only on the total quantity of gas which it is capable of adsorbing or absorbing, but also upon the concentration of the gas which it is required to eliminate from the air breathed. For very high concentrations the life of the canister may be only for a few minutes, while in very small concentrations it may be a matter of several hours before the canister becomes so saturated that gas breaks through to the facepiece. The time, concentration and nature of the gas for which the canister will afford protection should be known before one relies upon the gas mask in an atmosphere containing toxic gas or vapor. It should also be realized that *the canister type of gas mask is of no use except* in atmospheres containing a *sufficient amount of oxygen* to support life.

For protection in enclosures where there is not a sufficient supply of oxygen in the air to support life, an entirely different type of gas mask is required. In places such as coal mines where there is at times an insufficient supply of oxygen, the oxygen inhalator or oxygen breathing apparatus is employed. This is a type of mask which is completely enclosed and provided with a cylinder of compressed oxygen which is slowly released about the face of the wearer. No air from the outside can enter this mask.

Another type of mask employed where insufficient oxygen is present, is the hose tube mask. This consists of a facepiece such as the Army gas mask facepiece, to which is attached a long hose tube which extends to a source of pure air. This type of mask is useful for workers required to carry on in oil tanks or other enclosed places which either do not contain a sufficient supply of oxygen or else contain such high concentrations of vapors or gases that a canister would break down in an extremely short length of time.

The present efficiency and extensive use of gas masks in industry is due largely to the extensive researches and applications developed for the Army gas mask. Further extensive research and development will be required, how-

ever, before gas masks for either the Army or industry possess the life in storage and in use that is desired. The rubber parts of the gas mask, such as the facepiece and hose tube, deteriorate in storage. The use of rubber antioxidants and the regulation of storage conditions give promise of increasing the life of rubber but at the present time there is no certain solution of this problem. It is also desirable that the life and efficiency of the chemicals for canister filling be increased. Progress is constantly being made, however, and it is not improbable that new developments in industrial masks will assist in improving the Army gas mask, just as certain features of the Army mask have been adapted to industrial use.

When we consider the profound and demonstrated power that lurks in chemical and, in fact, in all branches of modern warfare, we realize the tremendous responsibility imposed on those who direct nations politically. For in their hands lies the power to keep the peace, or to loose these new, potent and merciless products of our civilization against our fellow mortals and brethren. Even the victors, if such there be, will stand aghast and weep.

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Colloid Chemistry and Geology *

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As descriptive mineralogical facts are to be treated separately,† we will here consider only some characteristic examples of dynamic phenomena. Since most materials may be dispersed colloidally, mineralogy must allocate many new names to colloidal minerals.

In treating geological dynamics, colloid science goes far outside the zone of colloidal dimensions. Colloid chemistry has in fact become a science dealing with phenomena of interfaces. Adsorbent and adsorbate do not necessarily have to be colloidal for colloid chemistry to consider the adsorption involved. It was only lack of appreciation of this fact that led G. Keppeler to say: "Although the general behavior of colloids and of clay parallel each other in all particulars, it is nevertheless remarkable that clay particles are mostly large enough to be microscopically visible."

CHANGES IN DISPERSION.

Mechanical Disintegration.

Technical experience shows that by purely mechanical means we get mainly a super-colloidal degree of dispersion. Grinding has its limitations. Thus the waves of the sea produce mainly minute grains of sand, though the grinding action is of immense duration. Shearing pressure is one of the effects hitherto not fully appreciated in geology. Even though the particles of a salt ground in a mortar may remain comparatively coarse, the researches of Tammann and Balarew indicate that there may be a disintegration of molecules at the granule surfaces; this would indicate a chemical effect.‡ The theory of waterfall electricity points this way (Lenard).

In many cases nature works with such tremendous forces that direct mechanical grinding into colloidal dimensions may be expected. The extent of this mechanical effect will generally be widened by the presence of materials which work like the inert dispergators used by von Weimarn and Plauson in the colloidal mill or mortar; finally chemical dispersion adds to the effect along the lines followed by Kužel in treating tungsten, which is, of course, no longer a purely mechanical effect. Besides this we must realize what happens in a volcanic eruption. Such tremendous dispersions as caused the eruption of Krakatoa to be followed by brilliant rosy dawns and sunsets, are to be ascribed rather to condensations from the gaseous state.§

* Translated by George O. Wild, New York.

† *See* the paper of C. Doelter in this volume. J. A.

‡ E. G. Acheson reported an evolution of hydrocarbon in small quantity in producing deflocculated or colloidal graphite. *See* his paper in this volume. Colloidal material formed on grinding may be continuously removed. J. A.

§ Professor R. Zsigmondy pointed out that under pressure water dissolves, or dissolves in, glass and silicate materials. Where these jelly-like solutions are suddenly released from pressure, as in the eruption of Mt. Pelée, they explode violently, yielding finely atomized particles which may settle so slowly that they continue to fall for weeks. The "nuage ardente" which practically annihilated the town of Martinique when the first outburst of Mt. Pelée occurred, was presumably composed mainly of the heavier particles mixed with finer ones; for part of the outburst appeared to be aimed directly at the town. J. A.

Baueritisation; Permutoidal Structure.

With silicates the ordinary sequence is from silicate to SiO_2 sol, *via* an intermediate molecular dispersion. Theoretically direct sol formation during decomposition is possible in case the primary SiO_2 particles are not too coherent in the original mineral.* Rinne assumed such a structure to be present frequently in his experiments on Baueritisation. A biotite could be disintegrated to such an extent that only the SiO_2 remained, still maintaining the exterior structure of the original biotite. There are, however, other possibilities; Ag obtained from AgCl by reduction with an aqueous reducing agent, also retains the original particle shape although the Ag-ions were previously separated.

Tammann, who pushed the idea of tempering so far as to assume that Au is atomically dispersed in Ag, found gold in microscopic crystals when he dissolved out the silver. A condensation had, therefore, occurred. Eggertz, who produced colloidal carbon solutions when he dissolved steel in acid, considered this as evidence of the most profound dispersion of the carbon; but his views were criticized. Similarly with Rinne's experiments the SiO_2 particles might have undergone a subsequent aggregation. Agerization produces, of course, enormously enlarged internal surface, an effect even more pronounced with siloxen, $Si_6O_3O_6$, made by Kautsky from potassium silicide. As in a book, crystal foils 1 to 2 molecules thick lie one on top of the other. Color solutions which are strongly adsorbed may penetrate into the interior of this "book" only *via* the cut edges. The topochemical forms of Kohlschütter may also be considered from the point of view of agerization: calcium oxide obtained by heating the oxalate to a red heat, has a larger internal surface and yields milk of lime more readily than does calcium oxide derived from the carbonate.†

With zeolites, which are of the greatest importance for the soil, the internal dispersity is the dominant factor. Rothmund taxed Wiegner with attributing base interchange to adsorption, while at the same time speaking of chemical equivalents. This apparent contradiction can be reconciled along the lines of K. H. Mayer's view regarding cellulose; with siloxen the surface is practically proportionate to the number of molecules.

AGEING.

With silicic acid the sequence of steps in ageing is from sol *via* jelly, opal, chalcedony, to quartz. In the course of time there is a closer approach of particles in the jelly, leading to pressure and to exudation of water, even in those cases where evaporation is out of question. Syneresis is thus a consequence of ageing.

Aging may proceed by various processes. Often (the Ostwald ripening, after Wilhelm Ostwald) the larger particles grow at the expense of the smaller ones, which have a higher solubility and vapor pressure.‡ Solution or vaporization is intermediate in the process. Rinne has thus explained globular schist formation in contact with plutonic rocks, various devitrifications (felsitization), and the formation of very coarsely granular deposits of rock salt.

* V. Kohlschütter has made an aluminium hydroxide colloidally dispersible in dilute HCl, by immersing alum crystals in caustic soda solution. *See also* paper on "grown" alumina by H. Wislicenus in Vol. I of this series. J. A.

† Metallic lead prepared by heating dry lead tartrate at the bottom of a test tube is so finely subdivided that it takes fire spontaneously when thrown out into the air. J. A.

‡ In this connection *see* "Solubility and the Size of Particles" by G. A. Hulett in Vol. I of this series. J. A.

The Wiegner Effect.

In a silver-sol stabilized by a protective colloid, R. Gross on allowing the sol to stand for several weeks observed precipitation of minute Ag crystals 10 mm. in diameter. He refers to collective crystallization and aims to explain by this phenomenon the growth of gold nuggets in alluvial deposits.

It is quite possible that we have here the effect found by Wiegner and Galecki, namely, that when a polydisperoid sol coagulates, submicrons will act as coagulation nuclei for amicrons. Flowing water brings highly dispersed gold into contact with larger gold particles. The shell-like formations found at times with gold nuggets seem to be allied structures.

A concentric shell-like structure was observed by Zemčzuzuv with Brazilian platinum concretion, which he believes were formed from aqueous colloidal Pt solutions. The Wiegner effect may also be of importance in connection with the formation of oöliths from other substances.

Fibrous minerals often give indications of having been formed from jellies; but the entire mass did not simultaneously form a gel. Mügge believes it much more probable that only the outmost layer of the growing mass was in this state. Soon thereafter came the transformation of this layer into crystal fibers. This view alone suffices to explain why rotund kidney-shaped pieces of hematite up to 40 cm. (18 inches) in diameter were not deformed by their own weight.*

According to Mügge hair-like exudations develop only on porous bases which feed the material for further growth. This form is observed with rocksalt, anhydrite, gypsum, Iceland spar, iron and copper sulfate. Cases exist, however, where the conditions predicated by Mügge are not realized: on exposing a glass plate covered with a layer of gelatin jelly to freezing, very short hair-like crystals of ice are at times formed, which, velvet-like, project from the surface of the jelly. Local dehydration of the gelatin produces pores, which then lead to hair formations.

A. Beutell presumed that hair-silver, which he made by heating Ag_2S in a vacuum, was produced by a slight decomposition into S vapor and Ag. The Ag is supposed to diffuse through the solid Ag_2S towards the cooler end. Since Vollmer found that the new structural units glide along the surface of a growing crystal, this view of the dynamics seems preferable.

Aggregates of gypsum, mica, cyanide, etc., composed of parallel fibers, which readily undergo translations, form a third group according to Mügge. Mechanical influence predominates here. By subjecting a gel to tension, fibers of chrysotile may be formed, often as long as 2 cm.; these may be split indefinitely into finer and finer fibers. The determination by Kurt H. Meyer, Mark, Katz and others that in materials such as gelatin, rubber, and cellulose unidimensional crystallites can be produced by torsion, throws new light on the problem dealt with by Mügge.†

Segregation Ores and Pyrosols.

When a melt cools, a material which was in true solution at a higher temperature may separate as a sol. Speed of cooling, growth of nuclei, viscosity, the position of the metastable limits of supersaturation, etc., are of importance here. Such segregation of ores are of frequent occurrence according to Schneiderhöhn. The great solvent power of copper pyrites for other ores in

* *See* paper on "Concretions" by H. Schade in Vol. II of this series. J. A.
† *See* papers on X-ray analysis, rubber and cellulose in this volume. J. A.

the liquid magmatic phase, is responsible for the numerous segregations found in the Natas mine in Southwest Africa, according to Reuning. With minerals which are not ores, the same process may lead to what minerologists considered until recently to be impurities in minerals and slags. W. Eitel has introduced them into science by calling them "development dispersoids."

It is quite possible that the sol is formed before the melt has completely set. If the viscosity is then very high, even particles as coarse as are found in the globular diorites may be kept afloat. The segregated material need not necessarily become solid. Thus J. Stanfield assumes that in certain magmas there is formed an intermediate emulsion of sulfide and oxide ores in silica. On further cooling this pyroemulsion becomes a suspension.

The dispersions of metallic silver in fused AgCl, of Pb in $PbCl_2$, Cd in $CdCl_2$, which R. Lorenz * termed pyrosols, were, upon a re-examination by W. Eitel, shown to be ionically, not colloidally, dispersed. The subhalide formed decomposes only after the setting of the melt, and then only does the metal appear in sol form, that is, as a pyronephelite. F. Blank found the same when he dissolved a metal in the melt of a different kind of salt, i.e. gold in sodium chloride. The conditions are similar to those obtaining in technical gold-ruby glass.

Blue Rocksalt.

Siedentopff advanced the theory that the color is due to colloidal metallic sodium, and he was able to produce the color by heating rocksalt in sodium vapor. Doelter † doubted the identity of these two forms, because their chemical and physical behavior is different. The reason for this divergence was explained by K. Przibram: natural salt contains an equivalent amount of free chlorine besides the colloidal sodium. The gas is lacking in the synthetic product of Siedentopff. Przibram calculated that a radioactive potassium salt must act over a period of 20,000 years to produce this blue color, which appears at such spots where the crystal lattice is deformed by foreign additions or by pressure. In an analogous manner G. O. Wild tried to explain the violet color of amethyst by colloidal silicon.

The general question as to how sodium particles can grow together within a solid crystal structure to form colloidal particles, may perhaps be answered in connection with the views advanced by Eggert, Leszynski, and others as to the latent image on photographic plates: the electron given off by the anion upon radiation does not necessarily need to jump to the neighboring ion, but it may wander about in the lattice and finally neutralize some distant metallic ion. Thus final neutralization may occur only in some distant location.

Transportation of Material.

Effects of Gravitation.

"The Movements of Coherent and Non-coherent Minerals," by V. Pollack, deals mainly with coarsely dispersed materials, sands down to turfs. Most generally motion is determined by a finer degree of dispersion, reaching the colloidal range which lies between the coarser material and binds it together.

An important step in the application of colloid chemistry to geology was the theory of *delta* formation by G. Bodländer in 1893. Sedimentation is determined not only by diminution in flow, but also by the aggregation of the

* *See* his paper in Vol. I of this series. J. A.
† *See* his paper in this volume. J. A.

free floating particles due to the higher electrolyte content of the sea-water. The aggregated particles settle more readily (Stokes' law).

In connection with this form of sedimentation, the principle of Wiegner and Galecki must be considered: particles which of themselves are not yet sufficiently aggregated to settle, may be attracted by larger particles and dragged down with them.

G. Goetz proposed a theory of dolomite formation: a colloidal mixture of colloidal carbonates of calcium and magnesium, protected by a colloidal impurity, is carried by rivers to coastal tidal flats, where electrolytic coagulation occurs.

Capillary effects do not generally appear in such simple form as most geologists and soil chemists imagine. An example of simple capillarity is the penetration of water into dried hydrophane. Rain, falling on dry soil, is partly influenced by gravitation. Osmotic effects are produced by the saline content of soils. Swelling is also to be considered.

Link, Kaiser, and others, properly lay great stress on capillarity in considering the origin of calciferous crusts in arid regions, desert lakes, or weathering of stones in buildings.* However, as soon as the pores are filled with water, diffusion of salts commences. The chemical aspect must also be given proper consideration: joint action of capillarity with chemical processes may lead to very complicated structures, which F. Runge, in 1857, considered to be proof of the "formative urge" of matter. They are partly conditioned by a local clogging of the capillaries by precipitate formation.

A long period of continuous operation is necessary to effect any important surface accumulation of material by the process of capillary rise. The incidentally essential evaporation of water results in concentration not only directly, but also indirectly by virtue of capillary transport.

Sols having risen by capillarity may coagulate irreversibly at the surface and remain there indefinitely. With true solutions a reverse diffusion is possible: on the other hand supersaturated solutions may also move upward even after cessation of capillary movement, providing nuclei have been formed higher up.

Laboratory experiments indicate that capillary rise is much more rapid than diffusion, so that the latter is negligible; but this holds true only for the initial filling of the capillaries. After that the speed of capillary rise depends on the rate of evaporation. Since solar heat is variable, the two processes compete with each other.

Colloids, rising incidently, may narrow or close the capillaries. Matter previously in true solution which may tend to form $CaCO_3$, SiO_2, $Fe(OH)_3$, etc., will act similarly.

J. T. Singewald advocated the capillary theory of the deposition of deposits of Chili saltpeter. W. L. Whitehead replied that in very fine-pored porcelain, capillary rises of over 8 meters were known, but that the range is less in a coarsely grained soil. With saltpeter, however, we must reckon with autogenous narrowing of the pores. In the case of an efflloresence of the scale left by evaporation, the same salt constitutes both the rising substance and the pores. Snow can absorb water by capillarity.

According to Atterberg, sand having (round) grains above 0.2 mm. in diameter gives pores too large to permit the operation of capillarity. It would be more proper to say, too large to fill the entire lumen of the interspaces with

* This phenomena is of widespread occurrence and is frequently referred to. *See*, e.g., H. Bechhold, "Kolloid-Z.," **27**, 29 (1920); W. Kraus, *Kolloid-Z.*, **28**, 161 (1921); J. Alexander, "Colloid Chemistry," New York, D. Van Nostrand Co., 1930, 3rd ed., p. 102-104. J. A.

water, because even with the larger grains we must consider the "bound" water, which F. Zunker divides into film water and pore water.* Sands having grains less than 0.2 mm. are generally classed as "impermeable," because water no longer flows through them; but impermeability is a relative term, because capillary transfer is still possible.

Diffusion.

Its importance for geology is even greater than that of capillarity, though its effects are for the most part not isolated, but exerted in conjunction with other factors.

Diffusion with chemical transformation giving rise to rhythmical precipitation, produces beautiful bands of gold in silica gels which E. Hatschek regards as typical of the development of banded gold in quartz. The outstanding example for a long time was an agate model involving the identical principle. With agate there is predicated a pre-existant silicic acid gel in which iron hydroxide was rhythmically precipitated as a result of diffusion phenomena. However, the author of this hypothesis long ago pointed out that many varieties of agate, especially the moss and tubular agates, do not necessarily imply a gel but a diffusion medium similar to waterglass. G. Link goes much too far in supposing now that in no case or only in exceptional cases is diffusion responsible for the development of the primary banding of agates. Reading between the lines it is evident that his criticism is directed mainly against the supposed pre-existence of a jelly-like medium. He believes that the layers were formed simultaneously with the deposition of the silica, which means that he assumes the older view of M. Bauer that geodes grew by the periodical addition of material. Unquestionably the assumption of an external rhythm greatly facilitates the explanation; but it is not essential. In 1858 Gergens tried to synthesize an iron silicate pseudomorphic with iron sulfate by immersing a crystal of the latter in waterglass. Instead, he obtained dendritic growths, tube-like formations which recall the structure of moss and tubular agates.† Close study of Gergen's experiments shows that when waterglass solution is precipitated by salts of metals or by acids diffusing into it, a banding of silicic acid may occur. In this case banding and growth occur simultaneously, as Link claims. Pre-existence of the jelly is not essential, but diffusion and rhythmic precipitation remain as in the previous case.

This shell-like structure develops by progressive ageing during its formation: by steady small contractions which take place in a direction contrary to growth. In case this action extends far around the tubes (silicate growths), it may lead to the formation of "fortress agate," which, in this case, has grown from inside outwardly (Fig. 1). In other cases of precipitation, the effect just described radiates also from the walls: centrifugal and centripetal formed bandings overlap (Fig. 2). In most cases there is only a centripetal growth (Fig. 3).

Certain band-like structures of iron oxide, frequently met with in sandstone, correspond to the silver chromate rings in gelatin jelly, which have been used as models for agates. They are very well developed at Münzenberg,

* The forces operative here may be divided thus: (1) Molecular forces of the order of 1,000 atmospheres; (2) capillary forces of the order of 3 or 4 atmospheres; (3) gravity. This corresponds roughly to the classification of soil water by George Bouyoucos, as follows:

Gravitational water	— "super-available"		
Free water	— very available		
Unfree Water	capillary-absorbed—slightly available		
	combined	solid solution hydration	—unavailable

J. A.

† *See* paper by S. Leduc in Vol. I, this series. J. A.

Hessen, Germany (Fig. 4). The jelly-like medium is here replaced by sand, the pores of which are greatly constricted by clay. In this medium iron hydroxide was rhythmically precipitated, perhaps by oxidation of a soluble ferrous salt by oxygen which penetrated from the surface through cracks and fissures.

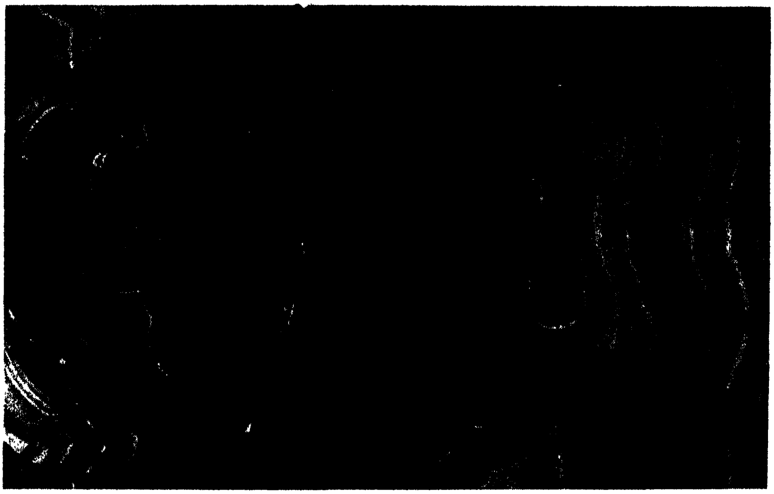

FIG. 1.—Agate Showing Centrifugal Growth (from Oberschlottwitz).

But we do not always have structural formation due to diffusion alone. The exterior rhythm as well as the capillary processes should not be overlooked when considering or explaining complicated structures such as the overlapping of two banded systems.

FIG. 2.—Agate Showing Centrifugal and Centripetal Banding.

Diffusion is possible even in the finished agate, for some agates are penetrated by black banding perpendicular to a crack subsequently formed. Oxygen, penetrating from this fissure, has transformed the ferrous iron to red ferric iron, often to the extent of several centimeters on both sides. This

indicates how there may be a new banding perpendicular to the original one. (*See* left half of Fig. 3.)

The drop in concentration which is the fundamental condition of diffusion of any substance, may also arise by its solidification at the containing walls, as when a magma cools. F. Rinne believes it possible "that a crystallization demixture may lead to a differentiation of a precursor, e.g., into a basic rind

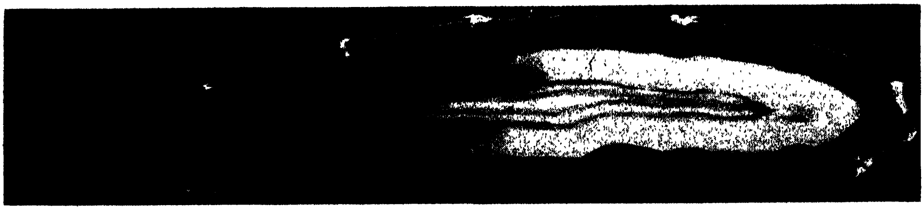

FIG. 3.—Brazilian Agate with Centripetal Banding.

and an acid interior, if the diffusion progresses toward the solidifying substance within geological order of size."

If, in a magma rich in silicic acid, free silicic acid disappears because calcium silicate is formed by contact with lime, active diffusion of silicic acid occurs in the highly viscous magma, accompanied by the much slower pene-

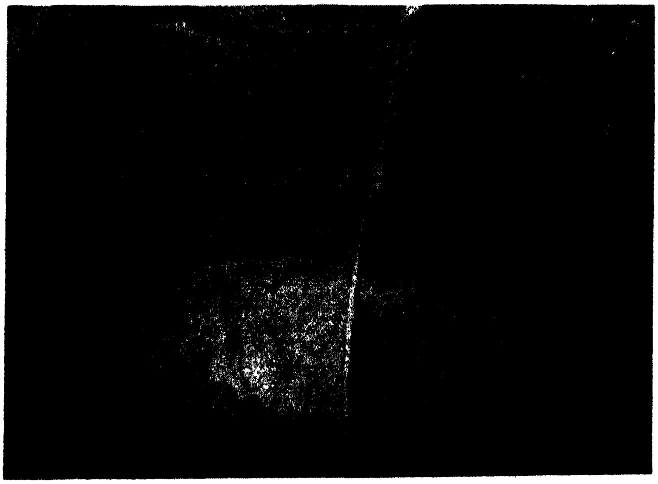

FIG. 4.—Rhythmic Precipitation in Sandstone (from Münzenberg).

tration of the silicic acid into the calcium silicate. Such diffusion in metamorphic solid systems is also the fundamental basis with many pseudomorphs.

A third possible cause of a drop in concentration is the elimination of a dissolved substance from the solution by adsorption. A jelly containing methylene blue and a piece of activated carbon will serve as a type. Around the carbon there is formed an almost completely colorless zone. Adsorption is not to be differentiated at all times from a chemical transformation. L. Michaelis and P. Rona, particularly, have sought evidence of chemical activity in cases of adsorption. P. Krusch assumed this view when he intro-

duced the idea of adsorption metasomatosis into the study of ore deposits. Thus the silicated nickel ores of the garnierite group are supposed to have been produced by the adsorption of dissolved Ni salts by the older gel minerals, which have been profoundly distorted because of impregnation. Similarly we can explain the formation of magnesite in serpentine.

One single salt seldom acts alone, but there is ordinarily a mixture of several salts. A jelly containing nitrate of silver into which a mixture of bichromate, chloride, bromide and iodide of sodium has diffused, may serve as a model. Bichromate heads the advance because the freshly formed chromate of silver is steadily decomposed by the halogen salts, whereupon diffusible chromate is set free. The iodide which is least soluble comes last.* According to this principle magnesia gets ahead of metalliferous salts in limestone. On the island of Nauru the calcium phosphate originating in guano is separated from the original coral by a sheet of dolomite.

Place-Interchange within Crystals.

The formation of pseudomorphs is no proof of the possibility of diffusion in crystals, for the changes here take place solely on the temporary interfaces within molecular range. Diffusion occurs within the distorted matter which no longer retains its normal lattice structure or which is composed of crystallites. In other cases it has always been demonstrated that the space lattice could not have been perfect when diffusion occurred within a crystal. Thus oriented inclusion of alkali silicate appeared when E. Warburg caused sodium or lithium to migrate electrolytically through rock-crystal. It will be necessary to evoke the differentiation between actual and ideal crystals if the special views of A. Smekal regarding vagrant ions are to be further expanded.

Contrary to what is found in many artificial crystals, many natural ones seem to approach ideal form. For this reason F. Paneth did not get an adsorption of radioactive substances on natural crystals of lead sulfide and barite, although his radiographic test was possible with crystals produced in the laboratory. It seems that his method is based on a very minute surface diffusion into the imperfect lattice.† G. v. Hevesy, on the basis of conductivity observations, also opposes the possibility of diffusion at low temperatures. Calcite and Chili saltpeter crystals conduct the current 50 times less effectively than do crystal aggregates, e.g. marble or a chilled saltpeter melt.

W. Jander draws the following outline to depict chemical reaction in the solid state, studied by Tammann and others (a and b are the two reacting components of two crystal faces in contact):

I. $a_3\ a_2\ a_1\ b_1\ b_2\ b_3$.
II. $a_3\ a_2\ (a_1\ b_1)\ b_2\ b_3$.

Here the vibration of the molecules about their places within the space lattice, have caused a_1 and b_1 to penetrate into each other's spheres of energy, thus leading to formation of the new compound within a single molecular layer. This must now turn over, giving an exchange of places:

III. $a_3\ a_2\ (b_1\ a_1)\ b_2\ b_3$. Then follow:
IV. $a_3\ (a_2\ b_1)\ (a_1\ b_2)\ b_3$; then
V. $(a_3\ b_1)\ (a_2\ b_2)\ (a_1\ b_3)$, etc.

* *See* J. Alexander, "Selective Adsorption and Differential Diffusion," *J. Am. Chem. Soc.*, **39**, 84 (1917).

† *See also* paper by McBain and Alexander in this volume. J. A.

This recalls the old electrolytic theory of Grotthus. Assuming the possibility of diffusion within the imperfect lattice, there is no need of assuming that more and more molecules must always turn over the further the reaction advances.

EDITOR'S NOTE.

It seems appropriate to mention here some consequences of the tremendous movement of finely dispersed mineral matter by winds and waters. Thus the prevalence of earthquakes in Japan has been attributed to the inexorable pressure exerted along the line of a fault in the earth's crust in the ocean bed, by clay brought down by the great rivers of China and flocculated by the salts of the sea. Reference to ancient geological shorelines will show how huge an area has been added to the United States by the Mississippi River, and analogous processes take place at the deltas of all great rivers.

The expeditions of the American Museum of Natural History into western China and Manchuria, led by Roy Chapman Andrews, have brought back evidence of the potent effects of wind and water on the soils and rocks there. The dust of such storms often reaches Japan, and Prof. Y. Wada stated that on March 4, 1915, such Chinese dust, with accumulated water films, made a deposit one quarter of an inch thick at Etchu Province, Japan.

The so-called "Sea of Darkness" in the Atlantic Ocean between Cape Verde Islands and the Canaries, probably owes its origin to dust storms from the Sahara Desert, especially between January and April. According to Hellman and Meimardus, a cyclonic storm central over Tunis about March 8-10, 1901, deposited about 150 million tons of dust on the African coast, and further great but incalculable amounts in the Mediterranean Sea. So high did the dust rise, that about one-third of the 1,800,000 tons deposited in Europe fell north of the Alps. E. R. Miller and A. W. Winchell traced a storm of dust-colored snow from Dubuque, Ia., to Chelsea, Vt., over an area of 100,000 square miles; the dust, apparently originating in the deserts of Arizona and New Mexico, must have been carried at high altitudes for over 1,000 miles before being brought down. The daily papers reported on December 19th, 1930, that a terrific storm swept over northern Algeria following a serious seven months drought; and on December 22nd the papers reported that a terrible fog (visibility 3 feet) had paralyzed London. Just prior to this (Nov. 27, 1930) a terrific sand-storm and hurricane blew over French Morocco, carrying a heavy deposit of yellow sand to the streets and foliage of Barcelona the next night. On the morning of Nov. 28th, a "mud-rain" fell in Paris, along the English Channel and the coast of Brittany. [*See* Jerome Alexander, *Science,* 63, 96 (1931)].

Volcanic action is another agency producing far-reaching dusts. Wilbur A. Nelson estimated that some time about the Cretaceous period a volcano in Tennessee spat up fifty cubic miles of material, which he traced as a deposit running about 450 miles north and south, and about 300 miles east and west. Bentonites have been made by analogous processes. A week after the initial explosion of Mt. Pelée which overwhelmed the town of Martinique, scientists found the air still full of fine ash, and ten weeks later another explosion scattered dust all over the West Indies. The eruption of Krakatoa in 1899 threw dust so high, that for three years it caused "golden" sunsets; the shock of this explosion is said to have passed three times around the earth, as indicated by barometric quivers.

This raises the question as to how far dusts may control solar heat and weather conditions. Dust particles serve as nuclei for the deposition of moisture, and fogs thus produced may materially alter climatic conditions. In fact, this has been mentioned as a material cause of glacial periods. The absorption of ultra-violet rays might have a further effect in altering the flora and fauna. Apart from its irritating effects on the respiratory tract, dust and smoke make city air much less "healthy" than country air. Abundant nuclei might also control the size of rain drops, and, to some degree, the distribution of rain by winds; for the finer drops are carried furthest. *See also* papers by Carl Barus, W. Gibbs, and W. J. Humphreys in Vol. I of this series.

Colloidal Minerals *

By Prof. Dr. Cornelius Doelter, University of Vienna.

Colloid chemistry, though a youthful science, has borne abundant fruit through the application of its methods to related sciences. Thus mineralogy, apparently concerned itself with crystalline matter and believed to exclude colloids, has likewise derived much benefit from the study of colloids.

Though the number of colloidal minerals is not large, yet genetically the chemistry of colloids is of great importance to mineralogy. It is being recognized more and more that many minerals originated as gels, and that the gels existing in the mineral kingdom, though difficult to recognize because of their instability, are much more widely distributed than has been supposed. Many syntheses, as I know from wide experience, have yielded only amorphous substances. In nature the same process appears to be selected, for in many cases metastable gels are produced which later, in a longer or shorter time, spontaneously or through the influence of certain other substances, change into crystalline form.

Therefore the importance of the chemistry of colloids inclines rather to the genesis of minerals than to the rather uncommon colloidal minerals themselves.[1]

Until recent years colloids have been almost entirely neglected by mineralogists. Amorphous minerals were distinguished from the crystallized ones, and the former were differentiated as hyaline or vitreous and porodine. But with the development of colloid chemistry, the attention of colloid chemists and mineralogists was directed to the noncrystalline minerals. In an address delivered by me in 1906,[2] as director of the Institute of Mineralogy in Vienna, the great importance of the chemistry of colloids to mineralogy was emphasized. In the year 1908 F. Cornu recognized porodine minerals as gels, and together with my pupils and myself investigated a number of colloidal minerals; owing to the untimely death of F. Cornu in 1909 his work on colloidal minerals remained unfinished.

In the development of this science the efforts of P. von Weimarn (formerly of St. Petersburg, now at Osaka, Japan) have been of much importance, but it is evident that a wide field still awaits the future investigator. The importance of colloidal minerals should not be overestimated, their number being small when compared to those having a crystalline texture; but it is certain that many minerals passed through the colloidal state.

Transformation of Colloidal Into Crystalline Minerals.

In mine workings, as well as in many other places, the formation of colloidal precipitates may be observed. But only a limited number of compounds have the property of enduring as gels for a long period; the majority soon become crystalline.

Hyaline-amorphous or vitreous substances likewise have the property of becoming crystalline. Devitrification may be observed in artificial as well as in

* Translated by Mr. O. G. Schlapp, Fort Madison, Iowa, and Dr. O. Ivan Lee, Jersey City, N. J.

natural or volcanic glass.* Microscopic investigation of the latter in all cases reveals some portions which have become devitrified, indicating the beginning of the process of crystallization. The rate of change in the case of vitreous substances appears to be insignificant. This is attested by the volcanic glasses, *obsidian* † and *perlite* which originated many thousands of years ago, but are now composed for the most part of vitreous matter. It may be observed that we are acquainted only with the glasses of recent geological periods. Pressure appears to promote crystallization.

Artificial glass may be changed to a crystallized or partly crystallized substance by subjecting it to a temperature slightly below fusion for a long time. The rate of crystallization of the compounds contained in the glass may be accelerated by decreasing the viscosity, which can be accomplished by the addition of substances like tungstic acid salts. Thus for example quartz and some aluminosilicates (felspar) may be obtained crystalline, while without such addition vitreous matter will result.

Vitreous rocks or volcanic glass from the earlier geological periods are not known, as I have already mentioned; but as they were probably produced then also, it seems likely that they were changed during subsequent ages. The semivitreous pitchstones, though, are found in the older formations; this proves that the rate of the transformation of glasses is relatively small, at all events when compared to that of gels.

Very many gels of the mineral kingdom have the property of changing quickly to crystalline substances; this is the reason why crystalline minerals are so much more numerous than colloidal ones. The stable condition of inorganic matter is the crystalline state, as is shown especially by the investigations of P. von Weimarn.[3] According to him, amorphous substances, and therefore colloids, are in reality crystalline. The opinion that amorphous phases are only concealed crystalline ones, dates back over a hundred years. The chemist, M. L. Frankenheim, especially defended the view that amorphous substances are really very finely crystalline; even glass was not excepted. P. von Weimarn endeavored to prove that all so-called amorphous substances differ from crystalline substances only in the degree of their dispersity. Precipitates like aluminum hydroxide and barium sulfate are, as he attempted to prove, in reality finely crystalline substances. He also announced the hypothesis that extremely fine rigid dispersed systems approach the liquid state. Extremely small crystals should, accordingly, have a form which becomes somewhat irregular as they approach the limit. According to him, the so-called colloidal properties become manifest gradually, in the same degree in which the rigid crystalline substance becomes finer or smaller.

In a treatise on the amorphous and crystalline state, I [4] referred to several colloidal precipitates which could only with difficulty be characterized as crystalline, as for example silicic acid hydrate gel which substance according to O. Bütschli possesses a characteristic honeycomb structure. But I agree with P. von Weimarn that every colloidal substance may be transformed to a crystalline body. Whether or not there are only crystalline substances, the so-called amorphous ones being crystalline in reality, can not be proved. In the above-cited treatise I have dwelt on the difficulty or impossibility of deciding for or against this view. The examination of ordinary carbon by the Roentgen spectroscopic method in comparison to graphite, by Debye and Scherrer would support the opinion of P. von Weimarn. At all events every gel or amorphous

* Randall, Rooksby and Cooper, *Trans. Soc. Glass Technology*, 14, 219 (1930), have demonstrated by X-ray spectrographic methods that glass contains and probably consists of colloidal crystals. J. A.
† Evidence of crystallization are quite visible in some specimens of obsidian from Yellowstone National Park, U. S. A. J. A.

precipitate and every colloidal mineral may be changed to a corresponding crystalline substance having the same chemical composition.

The transition of silicic acid gel to quartz as accomplished by E. Frémy and others, must not be classed with these changes, for the reason that a chemical change (a dehydration) was effected at the same time.

F. Cornu [5] announced the law of "isochemites" according to which every crystalline mineral may occur in the colloidal state and *vice versa*. But this is a consequence of the well-known fact that every substance may occur in all degrees of aggregation.

Methods of Transforming Colloidal Matter Into the Crystalline Modification.

The transformation, so far as can be observed, is spontaneous; but often the rate is very slow. In case of silicic acid it becomes nearly stationary or for all practical purposes equal to zero; but in other instances it is sometimes perceptible.

The rate of transformation is accelerated by shock (shaking), pressure and increase of temperature. The methods are practically the same as those which are employed to change finely crystalline into coarse-grained precipitates, or to increase the size of the crystals. The rate of transformation varies considerably with the substances experimented on. I was successful in converting a large number of colloidal precipitates into the crystalline form; for example $AL_2O_3 + H_2O$, $BaSO_4$, Sb_2S_3, ZnS, $Fe_2O_3 + H_2O$. The transformations were brought about by agitating mechanically for a period of several weeks.

The action of shock is much more intensive than that of pressure, although the same results may be obtained by the latter method, probably not in as marked a degree. Apparently the *rate* of crystallization is accelerated more by shock than by pressure; the transformation no doubt results in the same way in which a finely crystalline powder is changed to one of a coarser grain. In this transformation I consider the principle of P. Curie as controlling; that is the large crystals increase at the expense of the smaller ones.* From this we may conclude that minute invisible crystals were present also in the gel-like precipitates (like the foregoing) which continued to grow in size. P. von Weimarn is of the opinion that the minute globules which are observable in gels under the microscope and which show no signs of crystallinity under the most powerful magnification, are only apparently globular. This question is not easy to decide. In any case the final distinction between amorphous and crystalline precipitates depends upon the improvement of instruments—for the present therefore upon the delicacy of microscopic methods of research. It is possible that an examination of amorphous minerals by the X-ray spectrographic method will clear the matter.† Amorphous magnesite, hyalite or meerschaum is especially suitable for this purpose. If it is assumed that all amorphous bodies are only apparently amorphous but in reality crystalline bodies, they may be defined as crystalline substances whose rate of growth is very small, approaching infinity.

Since the methods are the same as those employed to convert finely crystalline precipitates into coarsely crystalline, all those operations which will give the latter result may be employed; for example augmenting the solubility by an increase of temperature and the like. Colloidal precipitates also become crystalline spontaneously. Very likely this phenomenon happens frequently

* Also called the Ostwald ripening. See paper by G. A. Hulett, Vol. I of this series. J. A.
† See paper by G. A. Clark in this volume, which includes many illuminating X-ray results. J. A.

in nature; but long periods of time are necessary. Occasionally crystalline and colloidal substances of the same chemical composition are found nearly adjacent in nature; therefore it appears probable that solution is necessary, as in the experiments, to bring about the change. Many minerals originated from precipitates which became crystalline in course of time. This may also apply to some minerals that occur as pseudomorphs, and in general to metamorphic formations that did not originate from molten magmas.

Distinguishing Crystalline from Colloidal Minerals.

In many cases it is very difficult to determine whether a given precipitate has a crystalline or a colloidal texture, and the same difficulty is met in distinguishing cryptocrystalline from colloidal minerals. In some cases the gel nature is plainly evident as for example with opal or amorphous magnesite; but in many others it is very difficult to make a decision. The structure should be observed especially under the microscope. If it resolves itself only into globules, one may safely decide it is a gel. I obtained amorphous precipitates in many syntheses of silicates that were composed of minute globules and showed no trace of crystallinity.*

The hypothesis of von Weimarn referred to above, that even the finest amorphous particles show an embryonic crystallinity, I shall refrain from discussing. But as some amorphous minerals, for example some opals, show double refraction due to strain, one would not be justified from the mere presence of double refraction to say a mineral is crystalline, although this theory would hold true in most cases. As they often vary slightly, other differences in properties generally cannot be employed to distinguish between colloids and crystalline forms, as for example the greater solubility of the colloidal modification compared to the crystalline, but in special cases this difference in solubility may be used.†

A very good method of distinguishing colloids depends on converting a gel into a sol; but in the case of minerals it fails for the reason that reversible mineral colloids are very rare. It has been stated that colloidal minerals show greater radio-activity; but this could not be used as a method of distinction. Under the heading "Clays" I shall discuss some of the other methods. In regard to structure, the quality which some aged gels have of occurring in laminated and in radial texture, may likewise be employed; but it is not reliable, as crystalline substances may occur having the same structure. One of the best, if not entirely conclusive, means of distinction, is that depending on the property of holding certain dyes; it will be discussed further on. Aside from several distinguishing characteristics of a subjective nature, a series of methods will have to be considered. According to Felix Cornu,[6] the following are characteristics of gels: dull luster, soapy or earthy texture, often spheroidal, grape or kidney-like (*botryoidal*) surface. But these qualities may also be found in crystalline minerals which originated from gels. At any rate, these external properties are not always characteristic. Some gels have a specific odor and adhere to the tongue. H. Stromme[7] and R. Aarnio have set up a series of methods which sometimes require modification; in addition they are linked up with the qualities of colloidal substances mainly in a transitional way. For these reasons a certain decision cannot always be reached.

* These globulites are probably masses of tiny crystals made globular by surface tension. Frequently they have polarity and form branching dendritic chains, which may snap into a large crystal lattice. See Vol. I of this series; also J. Alexander, "First Colloid Symposium Monograph," New York, Chemical Catalog Co., Inc., 1923. J. A.

† See paper on the mesomorphic states of matter by G. Friedel in Vol. I of this series, which deals with partially crystallized structure; also paper by G. A. Clark in this volume. J. A.

STAINING OR CHROMATIC METHOD.

The purely qualitative distinction by means of dyes suffices in many, but not all cases; it therefore offers no certain criterion. Treatises on this subject have been published by the following investigators: F. Cornu,[7] F. Hundeshagen,[8] E. Dittler,[9] K. Endell,[10] B. Sjollema,[11] P. Ehrenberg,[12] F. Grandjean.[13] Fibrous minerals like asbestos, also kaolin and other micro- or crypto-crystalline minerals, have the property of holding dyes. This method which will be of service in the case of clays should be considered more than a preliminary examination. It may be used under certain circumstances to determine colloidal minerals; but it is not infallible, as fibrous crystalline minerals may show the same property. The investigators cited above have tested the action of methyl orange, fuchsin B, acid violet, and the combination dyeing with methylene blue, fuchsin S, and methylene green, rhodamine B. Nearly all minerals acted the same as gelatinous silica; they took up the dyes from solution in a few hours, and did not readily give them up again. The mineral gels have typically chromatic properties so far as the property of coloration is concerned. Where a neutral triazide mixture (according to P. Ehrlich) was used, the basic dyes, methylene blue and methylene green, were almost exclusivly extracted from the solution. In case of equal concentration and quantity of the reacting agents the degree of coloration showed a great difference. Mineral gels of widely different chemical composition showed the same intensity of coloration, the crystalline varieties of the same composition dyed much slower and less intensely than the gel forms. F. Cornu has employed the chromatic method to determine the colloids contained in clays. The colloids contained in the soil are dyed black by a solution of fuchsin. K. Endell has employed the property of dyeing to determine the percentage of colloids in clays. From the intensity of the coloration the plasticity of clays may also be determined, as the plasticity depends upon the quantity of colloids. For distinguishing the colloidal portion from the crystalline, the chromatic method at all events has advantages.

It is especially important in the investigation of soils. Some older methods which are purely of a chemical analytical nature have been worked out by van Bemmelen.[14] Later D. J. Hissink [15] made improvements, but his method is suited only to clays, volcanic and laterite soils. The latter contain besides colloidal ingredients, quartz, crystalline silicates and small quantities of carbonates, phosphates, sulfates and chlorides. The colloidal ingredients include besides humus, colloidal oxide of iron, colloidal silica and colloidal silicates. However the latter are especially difficult to distinguish, for in them we have to do with a substance which resembles kaolin, and the chemical method gives very inexact results in their examination. In principle this method depends on separating the secondary silicates (those produced by weathering) from the crystalline and the quartz, by means of acids. HCl (gravity 1.19) is first employed, and then concentrated H_2SO_4 according to the method of A. Sabeck.[16] According to D. J. Hissink the quantity of the colloidal ingredients is determined from the portions resulting from the decomposition by treatment with HCl and H_2SO_4. Also the loosely bound and the fixed water and the content of humus are determined. Hisink has compared the results obtained by the method of van Bemmelen with those obtained by the chromatic method as modified by K. Endell; [17] the results were quite concordant. D. J. Hissink has referred to the centrifugal method of Sjollema in his address. Quantitative determination of the absorption by means of the above-mentioned dyes may give satisfactory results, because, as we have learned from the fore-

going investigations, crystalline minerals, when they react on dyes, color less easily than colloids. The method therefore appears to be serviceable.

DETERMINATION OF HYGROSCOPICITY.

The method was originated by Rodewell-Mitscherlich and consists of the following operations. The substance is dried in a vacuum desiccator in the presence of phosphorus pentoxide. For the latter a 10 per cent solution of H_2SO_4 is next substituted. A colloidal substance absorbs much water from a 10 per cent solution of H_2SO_4; a crystalline substance very little. The method appears applicable especially in the examination of farm soils and it is favored by agrogeologists.[18]

Graphs of Hydration and Dehydration.

Colloids give continuous graphs, while those of the crystalline hydrates show angles and appear step-like. The method has been improved especially by J. van Bemmelen,[19] but it is probably not applicable in general, as O. Ruff [20] and H. W. Fischer [21] obtained results in the case of hydrated oxide of iron which were not harmonious. We may also mention the investigations of G. Tschermak.[22] At all events the method must not be rejected at this time, as it appears to have possibilities.

The above-mentioned authors also recommend the suspension method of Th. Schloessing.[23] Finally F. Cornu [24] pointed out that some colloidal minerals swell while others shrink on being treated with certain reagents. In each case an absorption compound is formed. He refers to the investigations of V. Ebner on the optical reactions obtained with phenols, in which the direction of the double refraction is changed. It appears to me that this method can be used only to a very limited extent in distinguishing colloids from crystalline matter, and it has been mentioned chiefly for sake of completeness.

Occurrence of Minerals in Colloidal and Crystalline State.
Crystalline State.

Since substances in general, as is well known, may occur in the crystalline as well as in the colloidal form, it would not be safe to postulate two classes of minerals: colloidal and crystalline. Each mineral may occur theoretically in both forms. But examination of a list of the well-known minerals shows that only a very few occur in the colloidal as well as in the crystalline state. Very many minerals occur only in the crystalline form; but there are also others which are known only as colloids. Of the mineral compounds which are known in nature only in the crystalline state, many may be produced artificially as colloids. Among these are sulfur, iron, gold, silver, copper and sodium chloride (rock salt), a number of silicates, Sb_2S_3, ZnS, and many other sulfides, also calcium carbonate and some other carbonates. Most of the oxides which occur in nature may be produced in the colloidal form. Minerals which originate from a molten magma, like many of the silicates, are the only ones which cannot be produced in the colloidal modification. Besides the crystalline form of these silicates, the vitreous or amorphous form is likewise known as in the case of the felspars and similar minerals.

Because of the high rate of crystallization or growth, or, in general, because colloidal compounds have a tendency to change to the crystalline form, we are unable to find the colloids of such compounds in nature, although they are readily produced artificially. On the other hand, a large number of crystalline minerals are known which decompose through weathering; the products

of disintegration are colloids and these do not again change to the crystalline form, although the reversible transformation would be possible. I shall again refer to this matter in considering the formation of colloidal minerals. Among the minerals that exhibit, besides the crystalline phase, a colloidal one which is stable, I may mention magnesite, WS_4, FeS_2, $Fe_2O_3.H_2O$—as we see a very small list. But there are some also which are known only in the colloidal form; opal, bauxite, allophane, and wolkonskoite are examples. In addition there are some other minerals which are found both in the crystalline and colloidal modifications, but it is difficult to distinguish one from the other. Thus limonite is composed of both the colloidal and crystalline modifications, as is also the case with kaolin. Evidently these minerals originated as colloids and have become partly crystalline. The minerals which occur naturally only in the colloidal modification are mostly such as resulted from the decomposition of others. They may of course become crystalline, but some retain their original form.

The Water Content of Colloidal Minerals.

Most, but not all, colloidal minerals contain some water. This may be explained by the fact that gels have a tendency to absorb water at the time of their formation. This water content does not always fit into a stoichiometric formula, as it depends on the vapor pressure of the surrounding atmosphere and upon the temperature. The colloidal compounds of the mineral kingdom may be classed into those containing variable quantities and into those whose water content is in a molecular ratio.

Silicic acid may serve as example. Varieties of quartz in many cases originated as silicic acid gel [25] which contained variable quantities of water. In the course of time, however, a point is reached when the water content becomes stable.[26] Water-abstracting salts or a rise of temperature above 100° C. will produce crystallized quartz out of the hydrate. In the case of oxide of iron gel, the changes are similar; gelatinous oxide of iron is first produced with variable water content, then gradually a hydrate, and in the end, in the event of the withdrawal of water as in the foregoing, the anhydride is formed; but it has a crystalline structure. Colloidal minerals often contain adsorbed CO_2, H_2SO_4, phosphoric acid and the like. Therefore the chemical formula of such colloidal minerals which contain variable quantities of adsorbed substances, often cannot be established.

In general most colloidal minerals contain not a constant, but a variable quantity of water, as would be expected from their gel nature. The water content is partly water of adsorption, and in such a case does not bear a molecular ratio to the compound,* except where the process of crystallization has generally commenced. Refer to G. Tschermak's treatises published in the reports of the Vienna Academy on the behavior of silicic acid. His views, however, have not remained unchallenged.[27] The silicic acid which occurs in nature does not contain a constant quantity of water, but a noticeably variable one. In the formula of kaolin is included a fixed number of molecules of water; it seems likely, however, that this formula applies only to kaolin which has changed to the crystalline condition (*see also* under Adsorption).

Adsorption.

In the case of colloidal minerals, as generally with colloidal substances, in consequence of their highly dispersed condition, the specific surface proper-

* See paper by S. Utzino in Vol. I of this series, which describes experiments with Goethite. J. A.

ties play a great part. The most important reaction of the interface is adsorption. A solid interface adsorbs from an adjoining liquid or gaseous medium, the medium itself or possibly some solute. The interface can, however, adsorb only a limited quantity. Such an interface is then saturated and is of considerable importance. Different substances are adsorbed by different adsorbents in the same order. But this does not always happen in the case of crystalline adsorbents. Crystalline substances adsorb mostly colloids and conversely colloids especially prefer crystalloids.

Substances reduce surface tension to the degree in which they are adsorbed. Very important in the consideration of colloidal minerals is the foam-like structure of gels; but the view that this is the sole ultimate structure has been questioned in recent years and a different explanation is given by Zsigmondy and others. J. van Bemmelen [28] was the first to adopt this idea which was later investigated and confirmed by G. Quincke and O. Bütschli.[29] A consequence of this structure is found in the very large surface which gels have. Gels show the cavities and the partitions of the foam-like structure. The partitions are of elastic nature but become more rigid with increasing stability. Tabaschir is a gel which has been partly dehydrated. It is composed of a system of fine lamellae. The water contained in gels may be present in three different forms: (1) chemically bound, (2) confined within the texture (mechanically), (3) adsorbed at the interfaces of gel particles.* With constant pressure and an increase of temperature the confined absorbed water will be the first to pass off, and then that which was adsorbed.

J. van Bemmelen [30] found, on investigating the dehydration of silicic acid gels, an angle in the graph which illustrates the decrease of the water, an indication of the limit between the exit of the absorbed and the adsorbed water. Matters are somewhat different when a gel is placed in a salt solution. In consequence of the osmotic pressure, water diffuses from the gel and the latter shrivels and becomes harder. Therefore, a gel may be dehydrated in a salt solution. In nature where pure water is rare, but water contaminated by salts the rule, similar results are to be expected. In that case a very important factor, diffusion, asserts itself, the importance of which in a genetic relation has been brought into prominence by R. E. Liesegang.[31] † As this author treats of the subject in his work I may here refer to it very briefly. The partitions of the gel particles (foam particles) perform a significant part, as they adsorb dissolved substances, giving off adsorbed water in exchange. They will separate substances whose diffusive mobility differs.

R. E. Liesegang has succeeded in copying the structure of the Imatra stone by placing a crystal of calcium chloride in the center of a gel containing some soda. The remarkable structure of agates,[25] Liesegang accounts for by the diffusion of solutions of iron salts into silica gels, and the reaction with other substances which precipitate iron in the gel. Sometimes there are occurrences in nature that resemble the formation of Traube's cell, which may be produced by placing, for example, a granule of copper salt in a solution of ferrocyanide of potassium.‡ V. M. Graber [32] has tried to explain the occurrence of kernel concretions in Bohemian stratified sandstone in this way. J. van Bemmelen has directed attention to the great importance of adsorption in silicates that originate from the weathering of minerals. According to R. Marc, adsorption may also act as a catalyzing agent. The reactions which are made possible through adsorption may result between two adsorbed substances or between

* This corresponds to what Bouyoucos terms combined, unfree, and free water, e.g., in soils. J. A.
† *See* paper by R. E. Liesegang in Vol. I of this series. J. A.
‡ *See* paper by Stephane Leduc in Vol. I of this series; *also* R. E. Liesegang, in this volume. J. A.

an adsorbed and an adsorbing substance, in which case the latter does not react with the entire mass but only with the surface. J. van Bemmelen has given the name of adsorption compounds to the substances which result. If the outer liquid in this case is diluted, after an equilibrium has been established the equilibrium would not be restored by redissolving the adsorbed matter; consequently the adsorbed substance cannot be removed by washing. Kaolin for example has the property of adsorbing potassium but not sodium salts, and this potassium cannot be removed by washing. Such silicates, according to J. van Bemmelen, are especially important in laterite. These adsorption compounds can change to the crystalline form, and we then have to do with compounds which have already been accepted as molecular for the reason that the atomic formula obtained proved to be very complicated. I presume that ultramarine which is produced by fluxing, represents an adsorption compound of a silicate with a sulfide, but at the present time no proof is available. On the other hand some of the minerals that contain several acids in combination (as salts), e.g., thaumasite, might be adsorption compounds that originated as gels. Among colloidal minerals we find many which must be regarded as adsorption compounds. This will be taken up more in detail in treating the separate minerals.

Interaction between Solutions of Colloids and Crystalloids.

Many minerals originate from solutions of colloids. These solutions may be distinguished as lyophile and lyophobe. Lyophobe salts which persist are rare in the inorganic world, but these suspension colloids may have been of importance as intermediate transitional products. Lyophile sols are produced by chemical reactions, and from them gelatinous matter results, which gradually solidifies. Solutions of crystalloids may react with those of colloids. In cases where a gel-forming colloid is precipitated at the same time as a crystalline substance, a characteristic concentric laminated structure results, which is often to be seen in nature, for example in pisolite. Very similar are the structures of kidney and gall-stones, as has been shown by H. Schade.* Limonite, psilomelane, and botryoidal zircon show the same structure. It seems probable that the crystallization occurred in the presence of a gel.

The crystallizing matter may have been the gel itself which was transformed, or some other substance. The agates are characteristic of this structure and have been fully described by R. E. Liesegang;[25] their structure has also been artificially imitated by him. In these interchangeable reactions, adsorption takes a part. The crystalline substance adsorbs the colloidal, for example coloring matter. Sometimes alternating layers of colloidal and crystalline substances are deposited. These deposits are closely dependent on the nature of the gels.

General Remarks on the Genesis of Minerals from Colloids.

Some mineral bodies originated from sols. Hydrosols are not at all rare in nature. I may mention mine waters, rivers containing alluvium, and also ocean ooze. It is probable that they contributed towards the formation of minerals, but the subject has not yet been investigated. Hydrogels are of more importance and their origin may be accounted for as follows: (1) They may be produced from sols by the addition of electrolytes. The latter are

* See paper by H. Schade in Vol. II of this series. J. A.

contained not only in mine waters, but also in the waters of flowing streams. (2) They may originate through a change of temperature which causes flocculation. (3) Gels may be produced by the mutual precipitation of two sols. (4) They may be formed by means of weathering and decomposition of minerals, especially by the reciprocal action of the lithosphere and atmosphere, or more rarely the hydrosphere. Oxygen, CO_2 and water probably, influence the result in the main. Oxygen and CO_2 also act in solutions, as do also the contained electrolytes. In the dehydration of gels, salt solutions occupy an important place. (5) Finally gels may be produced through the influence or co-operation of organisms.

The Colloidal Coloring Matter of Minerals.

While some minerals have a color of their own (they are called *idiochromatic*) which depends on their chemical composition and crystalline structure, there are many others which owe their color to a pigment. Thus aluminum oxide which is colorless may occur in many different varieties like sapphire, ruby, etc., according to the pigment contained. The number of the colored minerals is large. Among these pigments there are some which occur in solid solution by being in mixture with isomorphic substances, but there are others that do not. It has been observed that the pigments which occur in solid solution have a greater stability in the presence of Roentgen, ultraviolet and radium-rays, etc. Likewise they show stability to change of temperature; while they may change, for example, on being heated, they resume their original color on cooling. A large number of minerals, however, show pigments which exhibit permanent changes when subjected to the action of the influences referred to. Colorings labile when exposed to changes of temperature and rays, are, in my opinion, produced by colloidal pigments. I have championed this view in a number of earlier treatises. It is difficult of course to produce any evidence for the colloidal nature of such pigments, but the analogy with colloids is very great, and in addition to this the other explanations which have been published appear very improbable. In the meantime we are dealing with an hypothesis, but one which appears to have much probability; other investigators have adopted the same views regarding these pigments.

In my work, "Das Radium und die Farben," which appeared in 1910, I have established my opinion, and advanced it since then in a number of treatises. Comparison shows the behavior of some pigmented minerals is at variance with others where no colloidal pigment may be expected to be present. The oft-repeated changes when minerals are exposed to the agencies named above, the sudden changes frequently observed as is usual with solutions of colloids and the reversibility of the color reactions are characteristic. Thus we may color sapphire yellow by the aid of radium rays, but the blue color may be restored with ultraviolet rays. Zircon takes a hyacinth color on exposure to radium rays, and resumes the original color with violet rays. Fluorspar becomes blue or violet with radium, and with ultraviolet rays returns to the original color. Quartz, barytes, celestine, topaz and many other minerals also show changes of color on exposure to radium rays. The Roentgen ray causes the same changes of color as the radium ray. An increase of temperature has the opposite effect, that is, the same as the ultraviolet ray. Some other explanations of the changes of color have also been published; of these I shall mention only the more recent ones. Jacob has expressed the opinion that it is due to a change in the molecular structure. But when one has observed that fluorite, for example, may assume four or

five different colors in succession, it does not seem likely that as many different molecular compounds for the substance could be formed at the same time. Likewise if rock salt be heated, a manifold change of color is observable which could hardly be traced to such complex compounds. It would seem more feasible to ascribe these color changes to chemical changes of the pigment, for example, to oxidation or reduction; but the fact that the effects are the same whether the agents act in a reducing or an oxidizing atmosphere would seem to contradict this. Anyway the possibility of an ionization exists, and this hypothesis cannot be dismissed summarily, although some things contradict this view, especially the large number of colorations that are brought about.

But even if this hypothesis is adopted, it seems likely that the pigment is a colloid, as crystalline substances are not affected. And this may be accounted for by the greater energy content of the colloidal phase as compared to the crystalline. We are therefore confronted with the possibility of a chemical action upon the colloidal pigment, or the phenomenon may be explained by a second hypothesis I shall now proceed to develop. It may be assumed that we have a highly dispersed substance under consideration; then we have the analog of a solution, and the color will depend upon the degree of the dispersity. The optical phenomena in solutions of colloids are a special case of the phenomena of turbid media, which are seen when a ray of light passes through a transparent medium in which are imbedded particles having an index of refraction different from that of the medium and whose dimensions are of the order of magnitude of light waves. A light wave passing through the hemogenous medium encounters an obstacle, the imbedded particle. It constitutes a center of disturbance which diffracts the light from its original course and disperses it in all directions. A diffraction of this kind is mostly selective. Incident light rays of different colors are diffracted to a different degree by the same particle.

If, for example, a ray of green light of fixed intensity impinges upon a particle of definite magnitude, we may ask what percentage of the intensity is radiated in all sidewise directions. Let us scrutinize, in particular, the direction which is at right angles to the course of the illuminating rays. This direction is chosen since it enables us to examine the light diffracted by the obstacle, excluding all direct light rays. Thus we may say in general that a small obstacle permits all waves to pass unhindered which are large in comparison to its dimensions. If, however, the waves of the illuminating rays are of the same order of magnitude as the dispersing particle, then the light rays will be dispersed selectively sidewise; waves which are smaller than the particle will also be dispersed. This subject may be referred to in treatises by G. Mie and F. Ehrenhaft. Calculations made by the latter investigator and his pupils demonstrate that the graph of the light diffracted at right angles, compared to the incident light as unit, has one or more maxima and is a function of the radius of the particles, the latter being taken as spheres of varying diameter. Consequently, if a homogeneous light wave impinges upon a number of particles gradually varying in size, one of them will be found to diffract the maximum quantity of the incident light at right angles. Larger and smaller particles will refract a smaller percentage of light of the same color in the same direction. The concept that a sphere whose specific tone approaches nearest to that of an incident light wave will also resonate best with it, thus becomes reality. It was justifiable to designate this selective color phenomena as *optical resonance*. Thus it was inferred that from graphs of optical resonance of submicroscopic silver particles, a sphere with a radius of

4×10^{-6} cm. would be influenced by light with a wave length of 400 $m\mu$ (blue light) more than any other, while light with a wave length of 650 $m\mu$ (orange light) has only a slight influence. These graphs demonstrate that the maximum of resonance of the particles to longer waves progresses with an increase in the radius of the particle. In the case of submicroscopic particles of sulfur, these graphs are especially interesting as they show that occasionally particles of different diameters resonate especially strong with the same wave.

The resonance graphs of sulfur particles have several maxima. Therefore to ascertain the color to be expected of a submicroscopic single particle, it is necessary to obtain from a host of graphs for a special material the light emission graphs for particles of various sizes. In this respect sulfur has an especial importance for minerals, as it is probable that some minerals owe their colors to sulfur. But, according to these findings, an admixture of sulfur may be the cause of very different colorations. Together with Prof. Ehrenhaft, Irene Parankiewicz determined the light emission graphs for sulfur particles of various sizes, by calculation from a host of graphs of the optical resonance. Sulfur particles having a radius of 8 to 9×10^{-6} cm. gave bluish violet light, of 9 to 11×10^{-6} cm. radius blue, of 11 to 12×10^{-6} cm. radius green, of 13 to 15×10^{-6} cm. radius yellow, and of 15 to 18×10^{-6} cm. radius orange, above the latter the natural color of sulfur itself appeared. It is evident, consequently, that different colorations may result from sulfur, as for example in ultramarine; but this is also the case with the metals Al, Li and Na. One and the same element, as has been shown with sulfur, may therefore produce many colors. This agrees with the observation that very different colors appear as a result of treatment with the various rays referred to, as with quartz, fluorite and other minerals. The frequently observed decolorization of tinted minerals may be explained by the collection into large agglomerates of the particles of the pigment. This phenomenon occurs in the case of minerals that have a natural color as well as with others which were colorless and have been colored with active rays (corundum, fluorite, zircon, quartz, apatite, etc.). A few remarks on the direction of the coloration in respect to the spectrum may be in place. Most minerals color in the direction from violet to red. This holds true for halite, topaz, boracite, sphalerite, silicate of zinc, sapphire, kunzite. The sulfates, celestine, barytes, and anglesite, and also apatite, and fluorite change color in an opposite sense. In the case of the sulfates as well as in that of the silicates which contain sulfur, ultramarine and hauyn, it seems plausible to accept sulfur as the pigment. It is therefore possible that different colors may occur in the same minerals. This agrees with experience in nature and likewise with colorations obtained by radiation. These phenomena may be caused by a difference in the degree of the dispersity of the pigment, which could then give different colorations. The colors of the different minerals agree with this supposition, as in case of fluorite which in nature may occur colored green, violet, rose and yellow. These shades may also be produced by radiation. To assume a different molecular compound for each color seems venturesome; likewise it does not appear probable that different degrees of oxidation could account for the different colors, for the reason that only a few elements form that number of different oxides. Liesegang [88] believes the degree of dispersity of colloidal pigments to be the cause of the variation of the natural colors, but not of those that are produced by radiation. But it appears clear that the natural colorations like those of quartz, fluorite, rock salt, etc., as well as those that are produced by radiation, owe their origin to the same cause. If, then, the theory is adopted for one type of coloration, it should be for the other also.

The objection that a flocculation by radiation would hardly be possible is unsound, for the reason that radiation no doubt causes occurrences like the dispersion of colloidal metals described by G. Bredig. At all events the explanation that the different colors of the same mineral are due to a difference in the degree of the dispersity of the pigment, comes nearer the truth than the other hypotheses. Of the hypotheses hitherto advanced, namely, that which was proposed by myself and the one which depends on chemical changes of the pigment for explanation and which I formerly advocated, the former seems more probable. Of course the hypothesis which corresponds only to the present state of the science may in the course of continued investigations be replaced by another which seems more probable. The investigations up to the present have given no satisfactory evidence regarding the chemical nature of pigments, but they have brought about the discarding of some opinions held earlier, for example that pigments are organic compounds or that violet is always due to manganese and red to chromium. But it can be asserted that the pigments have a close connection chemically with the minerals in which they are contained, either as a constituent part, or the relation may be of a genetic nature. In sulfates which are colored blue by radium, the presence of sulfur seems probable, especially as the color changes easily to yellow. The same thing happens in silicates which contain sulfur, e.g. hauynite, ultramarine (or lapis lazuli). In some cases there might be reduction to the metallic state which could assume different colors, as with fluoride, corundum, quartz. Consequently the colorations could be of the same nature as is produced by colloidal gold.

Importance of Protective Colloids in the Formation of Minerals.

Protective colloids may be efficacious in the formation of minerals. This phenomenon may be explained by protective colloids inhibiting the disintegration of compounds. As will be shown later, the presence of protective colloids is of importance in the formation of dolomite, for example. Silicic acid hydrate being widely disseminated may be mentioned as the protective colloid of prime importance; also organic substances may act as protective colloids. However little is known of them due to the small attention they have attracted. The influence of protective colloids should be looked for in places where minerals originate from silt, probably also in ocean ooze, in soils impregnated with humus, in swamps, peaty moors and the like. It will be necessary to consider with more attention not only gels but also sols. Although we are able only to investigate mineral gels we must also consider the sols which exist in mine drainage, in river waters, in silt, etc. (*See* footnote *infra.* J. A.)

Importance of Adsorption Compounds in Mineralogy.

We have already reviewed the importance of adsorption, but we must also distinguish simple adsorption from adsorption compounds. The compounds may be recognized by the fact that the equilibrium is able to adjust itself to the adsorption isotherm but this process is not reversible. If the outer fluid be diluted after reaching equilibrium, an equilibrium corresponding to the dilution cannot result from a re-solution of an adsorbed substance. The adsorbed substance cannot be removed by washing. R. Marc gives as example the adsorption of potassium salts by kaolin or alumina while sodium salts are not adsorbed. In this way the enrichment of potassium in the sedimentary rocks is explained; it may also apply to some other sedimentary

formation products. The adsorption compounds of electrolytes with a colloid may play an important part, especially in case of secondary silicates (produced by weathering) to which J. van Bemmelen has referred especially. Adsorption compounds are of great importance in clays and in similar cases where two gels were separated out at the same time. A mixture of two gels is obtained in such cases, which is homogeneous.

However this is not a purely mechanical mixture but an adsorption compound. I should here like to direct attention to another kind of compound. There are many minerals whose formulas point to compounds which are made up of two or more salts. The attempt has been made to define the formulas as molecular combinations of $A + nB$ in which A and B denote atomic combinations and n a fixed number. These formulas in many cases, however, do not appear to be unstrained. In reality the formulas should be $A + xB$ in which x represents a variable number. These compounds, which are not rare in the mineral kingdom, may have originated as colloids and may be adsorption compounds which have become crystalline. In many cases the ratio of A to B is variable and only because a molecular or even an atomic compound was assumed *a priori,* did a fixed ratio between A and B appear as a necessity; but with some silicates it actually happens.

The Importance of Colloids in Geology.

In sedimentary geology and in the much neglected sedimentary petrography, the investigation of colloidal minerals should be of great importance. Many sediments were formed out of colloidal minerals either by diagenesis or metamorphosis. On the bed of the ocean colloidal minerals are being formed at the present time. We shall consider the same more fully in special descriptions. Consequently some sediments still contain remnants of colloidal minerals. Of course it is conceivable, in view of the repeatedly mentioned tendency of colloids to change to the crystalline modification, that we find sedimentary rocks composed of crystalline minerals which originally were colloidal. In the sedimentary petrography of W. Wetzel [34] many minerals which were originally colloids are enumerated; the literature on this subject is also published. In this connection it should be observed that the attention of geologists and mineralogists has only recently been directed towards colloidal minerals. The colloidal ingredients of the sediments originate partly from the products of decomposition of rocks and partly from chemical precipitates. Organisms, especially bacteria, contribute towards the formation of some. Indeed minerals of which a colloidal modification was formerly hardly suspected, have according to all probability originated in nature as colloids; thus sulfur probably originated in nature as a colloid but changed to the rhombic form. Dolomite was probably formed as a colloid and calcite and limestone probably also originated out of calcium carbonate hydrate. All this may be accomplished artificially and its application to genetic conditions as they exist in nature does not seem very remote. Most of the phosphates were precipitated out of the ocean and of course in the colloidal form. On the bottom of the ocean the following minerals are formed: calcium carbonate, limonite, manganese minerals (*see* in special part) pyrite, magnetite, sulfates, all in the colloidal form. In some cases the colloidal structure remains to be established but in most the transformation has progressed towards the crystalline. The number of colloidal minerals in sediments will likely be augmented by further investigation. Even among the silicates, where they are least expected, colloidal minerals are known which originated out of the ocean; for example,

glaucolite and seladonite. Phillipsite which has been shown to be of marine origin by F. Koenigsberger likely originated in the colloidal form.*

Classification of Colloidal Minerals.

Sols and gels occur naturally and are classed with the minerals, but the mineral sols constitute a transitional form only, which has no stability in nature. Gels originated from them. This can be observed directly in mine drainage, in silt-containing streams and the like. In reality therefore we have no sol minerals to record. Nevertheless they are of the greatest importance genetically. Gels are formed out of sols and may be classified into reversible and irreversible-gels according to whether the change of the degree of dispersity, which causes coagulation, is reversible or not. Because of the presence of water in all parts of the earth's surface, as well as in the surface rock formations, reversible gels may easily be changed back to sols; they are consequently unstable and a reversible gel can only be observed in exceptional cases. Hitherto only a single reversible gel, ilsemannite, has been investigated; a number of treatises have been published about it. It will be referred to again further on. Yet it may be expected that in the course of further investigations other reversible gels will be discovered; perhaps oxide of iron hydrate will prove to be one.

Colloidal minerals appear in nature nearly always in the form of gels. As the time elapsed since their formation may be very great, but under certain conditions may also be comparatively short, chemical changes of the original substance may be caused by ageing, so that a definite formula cannot always be given. Different specimens of a gel of this kind may contain variable quantities of water. By adsorption they may have taken up variable quantities of water, carbon dioxide, phosphoric acid, etc. Some minerals in consequence do not have a formula which can be expressed in molecular quantities. But if time does not press, the substance in question may be permitted to adsorb until it is saturated, when a stoichiometric formula may be set up. Among colloidal minerals there are many which are composed of a mixture of gels, brought about by a mixed sol being precipitated by a common or joint electrolyte. In such a case a formula cannot be set up. However, if oppositely charged sols precipitate each other, compounds will be formed for which stoichiometric formulas can be established.[35]

Special Section.†

We will now consider the individual minerals which occur in nature as colloids. The sequence is the one usually followed in mineralogies: elements, sulfur compounds, oxysalts, halides.

Elements.

Colloidal elements are of slight stability; they rapidly transform themselves into the crystalline modification. Hence colloidal elements are seldom found as minerals, although it is very probable that most elements deposited from solutions were at first colloids, which were later transformed into crystalline minerals.

* *Biological segregations* must be considered. Thus, the ascidian *Phallusia* has a vanadium-containing blood; manganese occurs in mussels; copper in most molluscs. Just as coal is due to plant remains, so too, in some cases, relatively rare elements may be deposited with animal remains, whence they may later be leached. J. A.

† Translated by O. Ivan Lee, Jersey City, New Jersey.

Sulfur. According to F. Cornu,[36] sulfur separates from sulfurous hot springs as colloidal sulfur. Himmelbauer has shown that silicic acid can precipitate colloidal sulfur from H_2S and $(NH_4)_2S$. He suspects that the occurrence of sulfur at Radoboj in Croatia, where clay is intimately mixed with sulfur, is an example of the precipitation of sulfur by clay.

Carbon. As an example of amorphous carbon we have anthracite, which may be regarded as a colloid, together with the rest of the coals, although they are contaminated with other minerals. In any event the colloid originally formed is now represented by an amorphous substance. Scherrer and Debye from X-ray investigations conclude that the amorphous carbon is a very finely divided graphite.

Arsenic. Native arsenic, which frequently occurs in layered concentric fibrous forms having a radial structure, may well originate as a colloid, and perhaps also, *antimony*.

Gold. Elemental gold certainly was formed originally as a colloid although it is nowhere so found. E. Hatschek and A. L. Simon [37] explain the association of gold with quartz by assuming that a silicic acid gel has been impregnated by a gold salt, after which the gold salt (chloride) is reduced by carbon and perhaps carbonaceous substances, the gold being precipitated partly as a gel and partly crystallized. This view they have confirmed by experiments. In Australia, gold is associated with graphite. Likewise the enrichment of nuggets found in gold washings is confirmatory.

Iron. Concerning stable colloids in alloys see the several papers on Metals in this volume.

Oxides.

Opal. The most important mineral belonging here is opal and its different varieties: *hyalite, diatomite, kieselguhr, tripolite, randanite, menilite, melanophlogite,** *cacholong*. Opal has long been considered as a type of mineral gel. Opal is SiO_2 with an indefinite water content. However, other substances are absorbed by silicic acid, particularly sulfuric acid, and we sometimes find Al_2O_3 in the variety alumocalcite, beside CaO, and in many also, MgO, K_2O, Na_2O and NaCl. The sulfuric acid content in *melanophlogite* and in *sulfuricinite* is important, an adsorbed organic compound also being present.

Forcherite is colored yellow by adsorbed As_2S_3. (*See* below under sulfides.) *Fiorite* [38] contains in addition to silicic acid, adsorbed silicon fluoride. Many varieties of opal are colored, which A. Himmelbauer [39] has explained by mutual precipitation of oppositely charged salt solutions, for instance, iron oxide has positively charged particles, precipitatable by anions, while silicic acid has negatively charged particles whose precipitation is brought about by cations.[40]

Through ageing or through elevation of the temperature, opal parts with water, on which account the water content is a very variable one. Initially, *cacholong* is formed as the first member of a dehydration series; further loss of water gives *chalcedony* and finally *quartz*, the anhydride of silicic acid. Even chalcedony is crystalline. With the increase of crystallinity the loss of water also increases. The formation of opal rather than the crystalline varieties of silicic acid, occurs at temperatures under 100° C. Therefore J. Königsberger and A. Mueller [41] assume that opal can form at temperatures up to 200° C., which would be possible only in exceptional cases. In the presence of dehydrating salts, which frequently occur in nature, dehydrations

* The analysis of melanophogite gives 0.25 per cent to 2.8 per cent SrO. *See* in Rammelsberg, "Mineralchemie Supplement" II, 75.

set in at lower temperatures, as crystalline varieties of SiO_2 have certainly often been formed at little over 100° C. Towards dyes, opal is basophilic.

Stream tin is probably amorphous tin oxide.

Doelterite, according to A. Lacroix, is a colloidal titanium oxide, TiO_2.

Thorium Oxide. *Thorite,* $ThSiO_2$, yields on decomposition colloidal products, which contain also other adsorbed substances. *Meymacite* is a colloid of the same constitution as *tungstic ocher,* WO_3.

Gels of Iron Hydroxide. Ferric hydroxide easily assumes the gel form. Those produced in a laboratory fall into two groups, reddish-brown and yellow. J. van Bemmelen [42] considers them to be gels. O. Ruff [43] considered the yellow one to be a true hydrate and not an absorption compound. He found that the red colloid at high pressure quickly changes into a true hydrate and at 42.5° C. forms *limonite,* at 42° to 62.5° C. *goethite* and at higher temperature *hydrohematite.* The yellow colloid does not change its H_2O content at temperatures from 4° to 70° C. H. Fischer [44] did not get quite the same results: the yellow colloid he found to differ from the brown one, being difficultly soluble in acids. H. Fischer suspects that natural limonite is identical with the yellow colloid. He finds the red colloid tends to change into a red form poor in water.

Ferric hydroxides are very common. Limonite is partly colloidal, but as this is mostly an aged gel, there are many crystalline limonites. More recent formations, e.g., *bog iron ore* and the like, are often entirely colloidal. *Iron oölite* and other weathered products are also gels. It is interesting that in a certain quartz (iron-quartz) O. Mügge found ferric hydroxide gel as an inclusion. Many limonites contain sulfuric acid, phosphoric acid, and sometimes, according to F. Cornu,[45] vanadic acid, as absorption products. He assumes the following dehydration series: Limonite gel (*stilpnosiderite*), *xanthosiderite* brown botryoidal limonite, *hydrohematite, hematite.* It is possible that there is a series: hematite, ocherous xanthosiderite, limonite.

The red precipitate, formed by ammonia with solutions of iron salts, can be transformed into crystalline form. At a temperature from 60° to 70° C. the compound becomes dehydrated and at the same time crystallizes. The brown color changes to a blackish-brown. Probably goethite is formed. D. Marinkovich tried to transform ferric hydroxide gels into crystalline varieties. Simple drying gave semi-crystalline and crystalline products of variable water content; some consider this to be goethite, others believe it to be limonite. It is not necessary to use higher temperatures for these transformations.*

Aluminum Hydroxide Gels. The very common mineral *bauxite* and its variety, *laterite,* are colloids, which still possess their gel properties to a large degree, although they have partially transformed into the crystalline form. Their original gel state is still recognizable. Laterite is formed in the tropics by the action of rain on feldspar. Higher temperature may be the cause of the more rapid change into the crystalline hydrate $Al_2O_3.3H_2O$ than is the case with bauxite, whose gel-condition is in general easily recognizable. Bauxite is chemically the gel-hydrate of the alumina $Al_2O_3.nH_2O$, where "n" often is 1. Because of its gel character bauxite contains many absorption products, especially TiO_2, P_2O_5, SO_3, CO_2, V_2O_5. The alumina gel is mixed

* As pointed out in Vol. I of this series, p. 20, J. Alexander observed that the travertine at Mammoth Hot Springs at Yellowstone National Park, Wyoming, U. S. A., is initially colloidal, the newly deposited mineral showing a crypto-crystalline appearance. Sudden release from solution (consequent on cooling and release of CO_2) and the protective action of algal slime are factors leading to fine particle size. On ascending the hill older and older deposits are passed, until near the top where the deposits are estimated to be 20 to 30 thousand years old, marked crystal forms are found, the intermediate stages being clearly evident. *See also* J. Alexander, *Science.* J. A.

with aluminium silicate gel and with ferric hydroxide gel, $Fe_2O_3.nH_2O$. Because bauxite is industrially a very important mineral, its name has unfortunately been often given to mixtures of true bauxite with various other crystalline minerals, heretofore more properly termed "clay iron ore." I therefore proposed to call the gel-mineral *"bauxit"* (which is naturally contaminated by adsorption products), but to call the rock, which, besides bauxite, contains other minerals, e.g., kaolin and limonite, *"bauxitite"*. This would end the present-day confusion, whereby many substances, often quite different from each other, are termed "bauxite." Indeed, many of these substances often contain less than 50 per cent of aluminium hydroxide. Like all gels, bauxite also has the tendency to become crystalline, yielding *diaspore* and *hydragillite*. But in most cases there is some gel-substance present. The bauxite portion can be distinguished by staining methods, for the crystalline material does not take the dye. Bauxite is basophile. Alcohol differentiates bauxite from clay; there is no reaction with clay, but bauxite reacts pseudo-oxiphile. Bauxit is an irreversible aluminium hydroxide gel, mixed with ironhydroxide gel.

Manganese Oxides. Many manganese minerals consist of colloidal MnO_2 which, besides water, may have adsorbed many other substances. It seems that these minerals have been formed from some kind of mud, probably pelagic mud, and therefore salts have been adsorbed. Some contain Al, Fe, Ca, Cu, Co, Li, K and SiO_2. The respective minerals, previously considered to be crystalline, but whose colloidal nature was determined later, demand further investigation. They are therefore described but briefly. *Pyrolusite* (braunstein) is formed from crystallized manganite; also by reaction between $MnCl_2$ and $CaCO_3$. Similar minerals are the colloids *varvicite, wad,* and *lepidophaeite*. Wad becomes crystalline on ageing and is found in nodular or stalactitic form. It also forms "dendrites," and besides MnO_2 and H_2O it contains BaO as well. *Pelagite* (Church), apparently related to wad, consists of nodules of MnO_2, found by the Challenger expedition on the sea bottom. It exhibits brown concretions, containing also iron oxide and hydrated silicic acid. Lepidophaite contains adsorbed copper salts. *Lithiophorite* contains much CaO. *Rabdionite* contains iron oxide, copper and cobalt oxides. *Psilomelane* forms grape-like and stalactitic masses, which, originally colloidal, became crystalline upon ageing. In this state it is very hard, 5.5. It contains much BaO, K_2O and water in variable quantities. *Asbolite* contains, besides MnO, much H_2O and Co, Cu, Fe. *Cesarolite* is also a colloid; it is MnO with much water and adsorbed lead, besides Sb, As, Cu, Zn and Co. *Peloconite* and *melaconite* are mixtures of colloidal iron-, copper- and manganese hydroxides.

Sulfides.

Although few colloidal sulfides are known, many sulfide minerals were originally colloidal, but were soon transformed into crystalline modifications. Here belong: *Pyrrhotite, sphalerite, wurtzite, pyrite, marcasite, chalcopyrite* and others.

Sphalerite. Experiments show that it is difficult to get crystallized sphalerite; colloidal zinc sulfide is formed which can later be crystallized. It seems that this is the case in nature. Sphalerite is found in scaly and radial-fibrous aggregates and such minerals generally originate from the colloidal form. This seems to be true. Very recently, F. Bernauer tried to prove that a part of a layer of sphalerite has been formed by colloidal sedimentation. He dealt with lead-zinc deposits, especially those at Wiesloch (Baden, Ger-

many). Nevertheless, more research must be done before we are certain about the origin of zinc and lead sulfides from gels. There is also the possibility that radiate wurtzite has been formed from a gel.

Chalcopyrite. This might often have originated from a gel, probably in places where it is found as diagentic filler in clays.

Ferrous Sulfide. This is found in two crystallized forms, pyrite and marcasite. The latter is not very stable and easily transforms into sulfate. Schneiderhoehn found, in some marcasite aggregates, an agate-like structure, and it might follow from this that marcasite is prone to separate as gel. Whether marcasite or pyrite forms, depends on the temperature and composition of the solution. It is an open question, whether melnitkowgel, assumed by Br. Doss, really exists, and whether pyrite has been formed from it.

Patronite. This mineral (V_2S_5) is colloidal vanadium sulfide. There is an excess of sulfur, and probably the formula, as with pyrrhotite, is variable because the sulfide contains adsorbed sulfur. The analysis of W. F. Hillebrand [46] of the deposits in Peru gave the formula VS(?). Besides the chief constituents there have been found: Mo 0.18%, Fe 2.92%, Ni 1.87%. Silicic acid, carbon, titanic acid, alkali, aluminium hydroxide and iron oxide are possibly derived from the accompanying minerals. After extraction with hot water the proportion V : S is found to be 1 : 4.

Greenockite, Xanthochroite. Greenockite is CdS, partly crystallized, partly colloidal. The amorphous part is called xanthochroite.

Jordisite. This is colloidal molybdenum sulfide, MoS_2. We know very little about this mineral.

According to F. Cornu [47] the following are also colloidal: Ag_2S, black *argentite,* and amorphous HgS, which is obtained as a precipitate from mercury salts and which probably might be found in dense mercury ores. According to the same author, colloidal CuS and As_2S_3 also exist. The latter appears as the coloring substance in opals from Knittelfeld, in the so-called *forcherite,* and Auvergne (Bourboule), where I found it. Therefore it is probable that colloidal arsenic trisulfide exists in nature. The same holds true for Sb_2S_3. This is probably the *metastibinite* of G. Bekers.

Pyrrhotite (magnetkies). According to R. Canaval,[48] this mineral has separated, like other sulfides, in colloidal form. Pyrrhotite, as known, contains a variable excess of sulfur; therefore the formula is FeS,*n*S. Different analyses give a proportion of Fe : S from 7 : 8 to 11 : 12. We may assume a solid solution or an adsorption of sulfur by the colloidal FeS. As pyrrhotite has been precipitated from solutions by means of silicic acid gel, which itself became contaminated, this view is tenable.

Silicates.

Colloidal compounds occur in this, the most important mineral group; some are of special importance. Since silicates originated mainly from molten magmas where, of course, no colloids exist, the number of colloidal silicates must necessarily be small. We meet mainly with colloidal silicates formed by weathering. These are very important in agricultural chemistry. We shall consider here only the mineralogical individuals in this boundary zone.

Classification of silicate gels. The more common may be classified thus: copper silicate gels; serpentine gels; aluminium silicate gels; iron silicate gels; calcium silicate gels; nickel silicate gels.

Copper Silicate Gels. The main one is *chrysocolla,* an aged gel, which has partly become crystalline (formula, $CuSiO_3.2\ H_2O$). The dehydration product is *dioptase,* known in crystal form (H_2CuSiO_4). Chrysocolla is an

adsorption compound, for besides the above-mentioned components it contains CaO, MgO, ZnO, PbO, also CuCl and CO_2. E. Dittler found that chrysocolla can adsorb acid and basic dyes, the latter better than the former.

Cornuite is a copper-silicate, possibly belonging with chrysocolla. *Demidovite* is a gel, which can be considered to be an adsorption compound of copper silicate and copper phosphate. *Pilarite* is possibly also such an adsorption compound, which besides copper silicate contains much alumina and CaO.

Serpentine Gels. These are partly magnesium silicate, partly nickel silicate. Mineralogically, we should differentiate those related to talc, and those more similar to serpentine.

Meerschaum or Sepiolite. This is mainly a gel, which through ageing has become partly crystalline. F. Fersmann named the crystalline form *para-sepiolite,* but according to F. Zambonini,[49] who investigated its water content and dehydration curve, both varieties of sepiolite contain only adsorbed water. My own investigations show a transition between the two, showing that para-sepiolite is aged sepiolite gel. F. Zambonini found that alcohol or ammonia could be used instead of water in "rehydrating" the desiccated gel.* The formula of these colloids is $Mg_2Si_3O_8 . nH_2O$. H. Michel investigated the optical properties of the meerschaums and found that sepiolite shows true double refraction. I was able to synthesize gel-like sepiolite by action of magnesium sulfate in excess, on $MgSiO_3$ at about 70° to 80° C.

Spadaite is another gel-mineral, partly aged, therefore crystalline. The formula $H_4Mg_5Si_6O_{18}$. H_2O is not quite certain, as the water content varies. To this group belong also *quincite, aphrodite* and *gymnite* or *deweylite.* According to F. Zambonini, two different deweylites exist. Both are colloidal adsorption products; the dehydration curves are continuous. There are also ferriferous and nickeliferous gymnites (*iron gymnite* and *nickel gymnite*), which lead us to the nickel silicate gels. This by no means ends the series; we should note, in addition, the following: *stevensite* and *lucianite,* which correspond in their composition to crystallized talc.

Saponite is a characteristic gel, which because of its properties is called "Soapstone"; besides magnesium silicate, it contains water, alumina, lime and iron oxide. I give no formula for this on account of the uncertainty of its composition. Analogous minerals are: *bowlingite, cerolite, cathkinite, melopsite, hampshirite, gavite* and *hampdenite. Dermatine* is probably colloidal and related to serpentine; *webskyite* is a colloid.

Nickel Silicate Gels. *Garnierite* is a typical one (nickel-gymnite); here also belong: *genthite, noumeïte.* These are chemically intermediate between gymnite and sepiolite. Besides nickel, garnierite contains Mg, Fe, Al, Cu. Different analyses gave different results, because garnierite is a colloidal adsorption compound. As with all gels, the dehydration curve is continuous. Other nickel silicates are: *pimelite, roettisite,* $Ni_2Si_3O_8 . 2H_2O$, *sauligite, rewdanskite* ($R_3Si_2O_7 . nH_2O$, where R = Ni, Fe, Mg).

Of great importance for silicate nickel ores, and also on the question of formation of gel-minerals, is the work of W. Schornstein.[50] Reactions between metal salt solutions and gels exhibit, in addition to true adsorption, other processes, like ultrafiltration and formation of colloid complexes from

* It is of interest here to recall the pioneer work of Thomas Graham, who, in his paper "On the Properties of Silicic Acid and other Analogous Colloidal Substances" (*Proc. Roy. Soc., London,* June 16th, 1864); *Pogg. Ann.,* 123, 529-541 (1864), pointed out that certain fluids which do not pectize colloids, may partially or entirely displace the combined water of silicic acid gel. Among these are hydrochloric, nitric, acetic, sulfuric, and tartaric acids, glycerin, sugar syrup, and alcohol. He describes in detail the preparation of the *alcogel* and the *sulphogel.* (*See also,* "Colloids and the Ultramicroscope," by R. Zsigmondy, J. Alexander's translation, New York, J. Wiley & Sons, 1909, pp. 50-52.)

gel and metal salt solution (adsorption in another sense) if the metal salt solutions are hydrolized and therefore partly in colloidal solution. W. Schornstein formed a classification of the possibilities which might lead to the formation of mixed gels.

1. Mutual flocculation from mixed or complex sols.
2. Formation of a mixed gel from sol *A* and gel *B*.
3. Formation of mixed gels through adsorption of molecularly dissolved substances by gels.
4. Formation of mixed gels through infiltration of the solution of a substance *A* into a gel *B*.
5. Formation of mixed gels through chemical reaction between a substance *A* and a gel *B*.

Carbonates.

Colloidal carbonates exist as a water-free gel, something quite unusual, since almost all colloidal minerals contain water. *Amorphous magnesite,* an industrially important mineral, is formed from serpentine (magnesium hydrosilicate). It is pure white, differs from *crystalline magnesite* in containing no iron, and is often associated with opal. A. Himmelbauer (*loc. cit.*) observed at Kraubath (Styria), where it is found, quite soft masses of magnesite and silicic acid, which became hard on drying in the air. *Oölitic magnesite* also exists, this structure being characteristic of gels which have become crystalline by ageing. Amorphous magnesite stains with acid dyes, behaving as a base. It is widely distributed in the United States of America.

Gurhofite is supposed to be a colloidal form of dolomite, which is not very likely; it might be a mixture of amorphous magnesite with $CaCO_3$ and serpentine. Another gel is *giorgiosite,* related to the crystalline hydromagnesite. Its formula is given as: $(MgOH)_4Mg_2(CO_3)_4 \cdot 2H_2O$.

Colloidal Iron Carbonate. This originates in moors according to J. van Bemmelen, probably through reduction of limonite (iron hydroxide gel). The amorphous carbonate is formed where there are large deposits of vegetable detritus; it seems as if humus or humic acids are involved. R. Canaval and others suppose that the vegetable detritus exercises the rôle of a protective colloïd against crystallization.

White iron ore is probably a colloidal carbonate, from which *siderite* is formed. It is thought that its composition is: $FeCO_3xH_2O$. Krusch says that it forms strata in north German moors, especially in stratified sedimentary formations, but oxidizes easily. According to G. Krusch,[51] the carbonaceous iron carbonate, which is found in anthracite mines, leads to the hypothesis of such a colloidal precursor. *Vide* also C. Emeis. This seems to confirm the opinion of van Bemmelen.

Calcium carbonate. According to O. Lang, there is a calcium carbonate of the composition: $CaCO_3.xH_2O$, which has not been demonstrated as a true mineral, but which has been synthetically produced. It has been named *bütschliite.* It is found in sediments, but is already changed into the crystalline modification. According to W. Wetzel, it is also found as colloidal initial phase of the lime deposited by the *Septata.* About its synthesis *vide* O. Bütschli and Neuberg. I think it is highly probable that some calcium carbonates, especially radially fibrous and scaly ones, also oölite, have been formed from a colloidal modification of calcium carbonate.

Dolomite. This might also have a colloidal precursor, which gives rise to the crystalline form. B. Goetz[52] attributes the formation of the musselshell limestone deposits north of the Lothringer Haupsattels (Lothringen Mts.) to colloidal phases, especially dolomite. He thinks that calcium-magnesium carbonate under the protective effect of colloidal impurities, of the river water, silicic acid and vegetable slime got into the surface water of shallow sea near the coast and that there is at first electrolytic flocculation

of the mixed colloids, forming a colloidal precursor of dolomite. Without protective colloids there would be a separate decomposition of both carbonates, which would also happen in shallow sea water. This would also account for the failure of so many experiments to produce dolomite synthetically and in further research along this line, in my opinion, protective colloids should be used. Silicic acid would probably be most effective.

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Colloids in Glass

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Glass has been defined as a liquid mixture, or mutual solution of silicates (alone or with borates and other salts), whose viscosity is so high as to make it appear solid (solid solution) at ordinarily prevailing temperatures.

Solutions of silicate-soluble salts in glass resemble those of other combinations soluble in water,[1] in numerous instances. Auric compounds yield a yellow solution; cupric, blue; uranium, yellow by transmitted and fluorescent green by reflected light; the blue color produced by cobalt is like that obtained in strongly acid aqueous media; ferrous, green; ferric, yellow; manganous, colorless, as in dilute aqueous solution, and blue-green, rose or amethyst on oxidation; polysulfides, yellow to amber; chromium, green and yellow. Salts which are colorless in aqueous solution are also colorless in glass, if in the same state of oxidation.

Then we have the colloidal suspensions like the red, purple, blue and various colors produced by gold and other metals; opalescence by aluminum-bearing substances, stannic oxide, titanic oxide, phosphates, etc. Presence of strong electrolytes interferes here as in water solutions.[2]

What are the foundations for claiming the existence of colloidal suspensions in glass? Some of the experimental evidence is furnished here, and constitutes the reason for writing this chapter.

An example more frequently cited than any other, concerns the use of gold compounds. When gold was first used to color glass, it was introduced in colloidal form in Purple of Cassius (Kunkel, 1630-1703). Of course, this material dissolved in the melt, and to-day gold chloride is sprinkled on part of the batch (mixture of raw materials) and answers the same purpose. When gold-bearing glass, of fairly high concentration, is drawn from the pot it is yellow. Although some claim that this color is due to submicrons, the author feels that the gold is in true solution as an auric compound, since all gold-glass batches contain oxidizing agents. Bancroft states that colorless glass will result through chilling under either oxidizing or reducing conditions and that consequently the gold might be in true solution or so peptized by the glass that the colloidal particles are too small to have an effect on the beam of light.[3] The fact that a ruby glass may be produced by exposing the yellow or colorless glass to radium emanation seems to further substantiate the true-solution claim.[4] Reheating the yellow glass (colorless in more dilute or thin sections) in a reducing flame, first produces a pink color. Repeated, more prolonged or more intense heating will yield pink, red, purple, blue. After sufficient treatment, the glass looks brown, or livery, by reflected light and blue by transmitted, like a gold chloride solution in water, boiled with oxalic acid crystals, where the precipitate is brown and the supernatant liquid blue. The colors, in earlier stages of reduction, correspond to the succession observed when an aqueous solution of gold salt is reduced by phosphorus

dissolved in ether,* but glass offers the advantage that the colloidal particles in the solid solution are not free to move about as they do in water and so can be observed more easily under the ultramicroscope. Some of Zsigmondy's data follow:

SIZE OF GOLD PARTICLES IN GLASS.[5]

Glass	Color by Transmitted Light	Color of Particles	Cu. mm. Gold per cu. dm. Glass	Colorimetric Estimation	Size of Particle in $m\mu$	
					Based on Total Gold Content	Based on Colorimetric Determination
H	Pink	Light green	...	1.0	...	3.9– 6.9
F	Light red	Light green	8.0	4.4	9.3– 12.5	7.6–10.2
Cc	Red	Green	13.3	1.34	20.6– 32.8	9.6–15.3
Db	Blue to violet	Brass yellow	6.8	...	68. – 74.	...
Da	Blue	Copper red	6.8	...	68.8–103.	...
D	Livery	Deep yellow	10.1	...	131. –173.	...
A	Colorless	Golden yellow	12.6	...	487. –791.	...

As the gold content in all of the glasses differed, the estimation of the size of the particle was apparently not dependent on the quantity of metal present. That the size of colloidal gold particles of various colors in glass corresponds fairly well with their dimensions in aqueous media is also shown by Zsigmondy.[6] In this same publication experiments are described showing the effect of heat on color. A colorless strip of gold glass, which had been cooled very slowly, was reheated until it began to melt at one end, while the other end still remained cool. On cooling, the heated end was deep red and the color gradually diminished to colorless at the other end. Another piece of poorly prepared glass showed blue at the reheated end, shading through violet and red to colorless at the cold end. The poorly made specimen probably had more heat treatment in manufacture and before tests were made on the strip. Hence, larger colloidal particles formed, which colored the glass blue by transmitted light. Zsigmondy further points out that the "working temperature of colorless molten gold-ruby glass is several hundred degrees lower than the temperature at which it is melted," and that while most of the gold is in true solution, submicroscopic nuclei probably exist which serve as centers for further growth. He also calls attention to greater crystalloid solubility at 1,350° to 1,400° C. which accounts for the disappearance of color and return to true solution. That color production is in part dependent on cooling rate can be seen in pressed discs which are frequently lighter at the edges than in the center, due to variable conductance of the iron mold. It is claimed that color is not only dependent on the size of particles, but on their shape as well.[7]

One-tenth of one per cent of gold or less will color glass, the facility of color production depending on the composition of the glass. Lead-, tin- and barium-bearing glasses require less gold than lime-glass. It is said that increasing stannic oxide enhances uniformity of red color and minimizes blue formation.[8]

And now a bit of comment on the author's personal experiences. A gold ruby lead-glass was reproduced repeatedly for commercial use in fairly large-sized melts with good results. The color was uniform. In some small scale

* This was Faraday's method for producing colloidal gold. M. Faraday, *Phil. Trans.*, 1857, p. 154. J. A.

investigations as to the possibility of changing the color intensity, melts were made in covered Battersea crucibles. Their contents were poured into iron molds, forming flat buttons. These buttons were placed on asbestos board in an electric muffle furnace and heated up slowly until the glass melted, when the current was shut off and the furnace allowed to cool very slowly to room temperature. A set of buttons from a single crucible all showed nearly every color of the rainbow. Nor were the colors similarly located in the various discs. While these pieces constitute interesting museum specimens, the results are puzzling.*

The controversy between advocates of the cuprous-oxide and colloidal-copper theories concerning copper-red glasses eliminates them from our discussion. The matter is apparently unsettled.[9]

Selenium glasses appear black when drawn from the pot. On cooling, they may become colorless, slightly opalescent, yellow, orange, pale red or deeper red, depending on the alkalinity of the batch and the unvolatilized selenium remaining in the glass. Batches for selenium glass usually contain sand, zinc oxide, alone or in partial substitution for lime (lead compounds are rarely used with the sulfur family elements); potassium carbonate, alone or partly replacing sodium carbonate; antimony trioxide or cadmium sulfide; and a reducing agent, such as carbon, flour or sugar. Selenium is introduced as element (black or red form), or as sodium selenite. Whether introduced as element or compound, a sufficient amount of reducing agent insures conversion to element. When the glass is reheated, it again turns black and on cooling assumes an orange-red to a garnet shade, depending on the selenium content and heat treatment. High alkali produces a deeper shade. The deep red glasses show no colloidal particles in the ultramicroscope, so the color, especially since it is deeper with higher alkali content, is probably due to polyselenides,[10] just as the yellow or amber color with sulfur or reduced sulfates is due to sulfide or polysulfide formation. In salmon pink, opalescent and almost colorless specimens of selenium glass, colloidal particles may be seen. The reaction is represented as follows:

$$\text{"}3Na_2O + (2n + 1)Se \rightleftarrows 2Na_2Se_n + Na_2SeO_3$$

the equilibrium being shifted to the left at high temperatures and in mixtures rich in SiO_2, and to the right at lower temperatures and in mixtures richer in alkali." [11] The colloidal particles are said to be less than 40 $m\mu$ diameter.

While discussing the effect of selenium, it might be well to include the related elements, sulfur and tellurium. Sulfur and tellurium act as coloring agents under reducing conditions similar to those mentioned for selenium, forming polysulfides and polytellurides, which color the glass yellow and red, respectively. Considering the sulfur family, we may say that the color of the glass varies from yellow to red progressively with increasing atomic weight of the elements, alkalinity of the batch, and reducing conditions. Before reduction, or through subsequent heating and oxidation, or with increasing acidity of the glass, or with increasing viscosity of the glass (dependent on composition) the colloid-forming tendency progresses in the sulfur family with increasing atomic weight.[12] Sulfur and tellurium glasses which display colloidal phenomena are blue.

Soda glasses are colored blue to violet by X-rays and radium emanation,

* Differences in the initial chilling may have produced differences in the number of crystallization centers or nuclei, which, by subsequent growth determine the size and color of the gold aggregates. *See* G. Tammann, *Z. Elektrochem.* 10, 532 (1904); also "States of Aggregation" (translated by Robt. F. Mehl), New York, D. Van Nostrand Co., Inc., 1925. J. A.

and potash glasses brown. The sodium color closely resembles that of blue rock salt. This color has been produced in the laboratory by exposing salt crystals to radium emanation, cathode rays or sodium vapor.[13] The coloring of quartz and gems by ultra-violet light and radium is common knowledge to-day.[14]

The dichroic effect seen in aqueous solutions of chromic salts and in the mineral Alexandrite has been obtained in glass by the writer. The color in aqueous media has been attributed to colloidal phenomena, and the color of the glass closely resembles this. If two cells containing the green chromium solution are superimposed, the transmitted light is dark red. Superimposed pieces of the above-mentioned chrome-green glass display the same phenomenon. (*See* Ref. 1.)

Platinum and other chemically inactive metals may color glass. The author has found that platinum electrodes, in molten soda-lime glass subjected to an electric current, will discolor the glass near the electrodes if the current frequency is not sufficiently high. While these glasses have not been examined ultramicroscopically, the author feels that the platinum is in colloidal suspension, as the conductivity cell was filled with broken glass towards which platinum should prove inert after the glass had melted.

Opalescence is considered a colloidal phenomenon.[15] This is produced in glasses through the introduction of arsenious oxide, stannic oxide, calcium phosphate, titanium oxide, cryolite, or mixtures of aluminum- and fluorine-bearing compounds. The author's researches in this field have been confined largely to alumina-bearing glasses and it has been interesting to observe the effects of various agencies on the colloid. It was found that fused electrolytes, like NaCl and Na_2SO_4 dissolved in opal glasses, destroyed opalescence, just as dissolved salts would destroy it in aqueous media, and produced alabaster glasses in which opalescence was no longer perceptible, the glasses transmitting white light instead of fiery light.[16]

In alabaster glasses, the suspended particles are larger than in opal glasses, in fact so much larger that the phenomenon of opalescence disappears and white light is transmitted. Opal glasses behave like colored glasses which owe their color to the size of the suspended particles. If a light opal glass is reheated and cooled, the color intensity increases. The amount, degree and length of reheating determines the color and size of particles. As is the case with metal-colloid colors, true solution is effected if the glass is subjected to prolonged heating above its melting point. Even alabaster glasses may lose their color or become opalescent under these conditions.

Aqueous suspension alumina is a positive colloid. That NaCl dissolved in molten soda-lime glass, ionizes and increases the electrical conductivity, has been shown through recently conducted researches in the author's laboratory. (*See* Ref. 2.) In these investigations 0.95 per cent and 1.41 per cent, respectively, of sodium chloride was added to the glass and the conductivity studied above 750° C. While the conductivity does not correspond to that of an equal concentration in water, results compared with those obtained for the conductivity of fused mixed salts [17] indicate ionization of the NaCl in molten soda-lime glass. The author concludes, therefore, that opalescence in alumina-bearing glasses free from dissolved chlorides or sulfates is due to a positive colloid unaffected by the positive sodium and other metal ions present. Further, that when alkali chlorides or sulfates are added, the negative chloride or sulfate ions cause precipitation and an alabaster glass results.

An investigation of the history of clouded glasses indicates that as far back as the seventeenth century, or possibly earlier, and until the manu-

facture of salt-free and sulfate-free alkali carbonates was perfected, all clouded glasses were alabaster and displayed little or no opalescence. (*See* Ref. 16.) Natural and LeBlanc alkali carbonates contained sulfates and chlorides, and prevented opalescence, but with the introduction of pure potassium carbonate from Stassfurt and sodium carbonate made by the Solvay process, opal glasses came into being. It is interesting to note that with the advent of opal glasses, the art of making alabaster glass was lost for the time being, and that when the author began his work in the glass field in 1902, the production of this type of glass was his first problem.[18] The effect was produced by adding salt to an opal batch, and later with salt cake and other sulfates and chlorides. Leave these out of the batch and the glasses are opalescent.

Next, another observation must be recorded which is of interest. The alabaster effect failed to materialize unless an oxidizing agent was present in the batch. In other words, a batch containing salt yielded no opacity in the glass unless a nitrate was employed. When sulfates were used instead of chlorides, their partial decomposition yielded the necessary oxygen. Nitrates without chlorides insured opalescence but failed to produce the alabaster effect. It was also found that opal or alabaster glasses which had become transparent through prolonged heating above the melting point, would regain their color if air was blown through the molten glass which was next allowed to cool. What does this mean? Is it an argument against the theory that opalescence in glass is due to colloidal suspensions and that these are precipitated or congealed into larger particles through the influence of chlorides or sulfates? The author thinks not. The high temperature of molten glass, if this is heated too long, may result in the formation of aluminites, aluminates, or aluminum silicates or borates, which enter true solution and yield a clear glass. Oxidizing agents and air probably cause a transformation in these compounds with the formation of colloidal Al_2O_3. The ionized chlorides or sulfates then precipitate the alumina. Industry has recently utilized the oxidation-precipitation theory. A glass that is crystal-clear when gathered is rendered opal or even white in parts, by subjecting them to an oxidizing flame.

Now, what may seem like an exception must be cited. The newer zinc-aluminum, boro-silicate, fluoride, alabaster glasses may be made with or without an oxidizing agent, in fact with the reducing agent, arsenious oxide, present. Zinc is distinctly amphoteric. What its influence is in these glasses must still be determined.

Should fluorescence be considered under colloids? The author feels that fluorescence, like that produced by uranium compounds in glass, is due to a state of division and that particles between molecular and colloidal dimensions are present. Studies on the effects of oxidation and reduction, and of electrolytes in solution in the glass are under way in the author's laboratory, and observations made thus far prompt the prediction that fluorescence of the type cited can be destroyed like opalescence. This may lead to establishing a theory that fluorescence, like opalescence, is due to particle size.

Colloids in enamels and other decorative materials have not been discussed in this chapter as the author feels that this topic could best be developed by a specialist in enamels. In conclusion reference should, however, be made to mirrors, in which the silver film, deposited on glass from ammoniacal silver nitrate by formaldehyde[19] and other reducing agents is of colloidal thickness as it appears blue by transmitted light.

If reference to colloidal effects in glass by substances other than those mentioned in the chapter has been omitted, this has been done because the

information appearing in technical publications is controversial or insufficiently established.

It can be said, in conclusion, that glass may contain elements and compounds in colloidal suspension and that, except for freedom of motion, colloids in glass are similar to those in liquid media and subject to the same laws which govern them.

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Some Colloidal Properties of Sodium Silicate Solutions

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At room temperatures a solution of silicate of soda containing 36 per cent $Na_2O:3.9SiO_2$ is a stiff jelly into which one can easily thrust his fingers. The material has low tensile strength and is friable so that pieces can be separated from the main body of the jelly. If such a separated piece is molded into a ball, it will show great elasticity if bounced. In spite of this, the ball will slowly flow out if allowed to remain undisturbed.

In contrast to this a 36 per cent solution of $Na_2O:1.7SiO_2$ is a liquid which flows readily and easily. If it is concentrated until it contains approximately 62.5 per cent solids, this solution becomes a stiff heavy mass which flows very, very slowly. Portions of it can only be separated with great difficulty because it is extremely tacky and has high tensile strength. A ball made of this material will not bounce but flattens at the point at which it strikes.

Preparation.

These two examples illustrate the range in properties which are possible with silicates of soda. Although crystalline sodium silicates of definite chemical composition are known, the colloidal solutions are much more widely used. The latter do not follow the laws of definite or multiple proportions but are made to arbitrary standards set by the manufacturer.

The different silicates are prepared by fusing sodium carbonate with the desired amount of pure silica sand. When nearly equimolecular proportions of these materials are used, the product is largely crystalline Na_2SiO_3. However, if more sand is used, a glass will be formed. This can be dissolved in water as long as the silica does not greatly exceed four molecules to one of carbonate,[1] although, even within this range, special hydration is necessary to put the more silicious fusions into solution. For example, when glass of the composition $Na_2O:3.25SiO_2$ is powdered and boiled with water, very little glass is dissolved. If some of the same powder is exposed to an atmosphere of steam before being put into the water, it will dissolve completely in a few minutes.

Viscosity.

The properties of the solutions made from these glasses are dependent on the concentration and on the ratio of sodium oxide to silica. This may be illustrated by the viscosity relations. Figure 1 gives the change in viscosity with concentration for solutions of five different $Na_2O:SiO_2$ ratios. In every case at low concentrations the viscosity increases only slightly as the total solids increase. Then there is a point where the increase becomes greater and finally rises rapidly. The sharpness of the break and the slope of the final curve are both dependent on the $Na_2O:SiO_2$ ratio. The more silicious silicates change more rapidly than the more alkaline ones. Thus, to raise

the viscosity from 50 to 7,000 centipoises the concentration must be increased from 33.5 to 50.0 per cent solids with $Na_2O : 1.7SiO_2$ but only from 30 to 33.6 per cent with $Na_2O : 3.9SiO_2$. Above 38 per cent solids the minimum viscosity at a given concentration is obtained with solutions in which the ratio of Na_2O to SiO_2 is between 1 : 2.0 and 1 : 2.5 (Fig. 2).

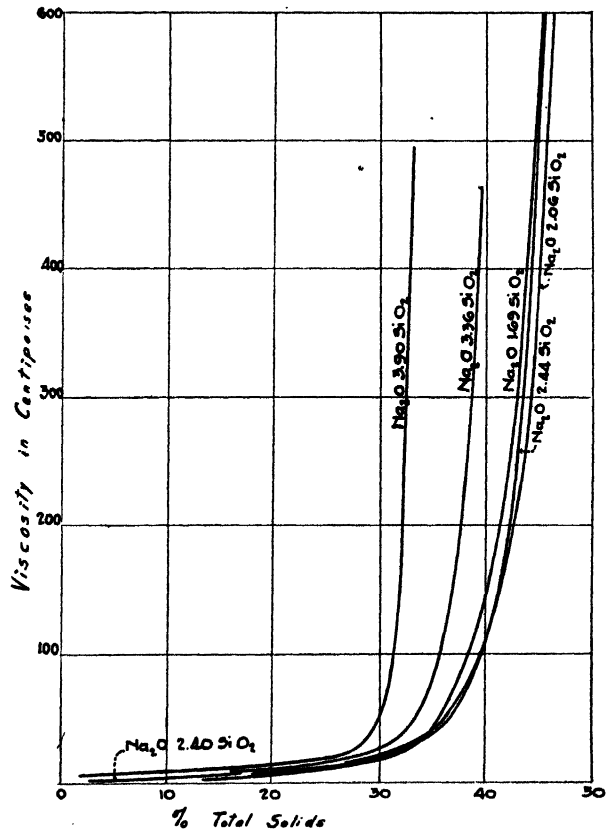

Fig. 1.

Although this property is affected by the sodium oxide content, it is primarily controlled by the silica content. The rapid increase in viscosity in all the silicate solutions occurs when the concentration of silica is between 22 and 28 per cent (Fig. 3).

Adhesive Uses.

Sodium silicate solutions are widely used as adhesives, particularly for corrugated and solid fiber container boards, wallboards, and for asbestos products. Silicates varying in ratio from $Na_2O : 2.7SiO_2$ to $Na_2O : 4SiO_2$ furnish most of the adhesive solutions. Silicates more alkaline than $Na_2O : 2.7SiO_2$ are more tacky but they set very slowly and their high alkalinities make them unsatisfactory for use with many materials.

The manufacture of solid fiber board is an example of the use as an

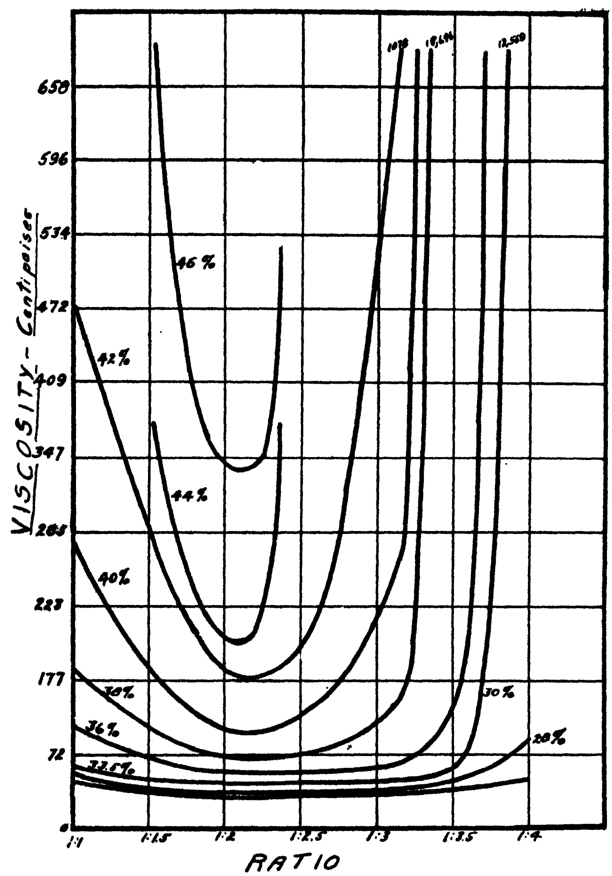

FIG. 2.

adhesive. (*See* Figs. 4 and 5.) Chip paper is unrolled and pulled through a bath of silicate. The excess of the latter is removed by passing between rolls and then a liner of strong paper, such as jute or kraft, is applied to each side. The resulting combined board then passes through a series of pressure rolls and over carrying rolls to a cutter. Even with traveling cutters there is some buckling and with stationary cutters the freshly combined board is subjected to great strain. The board may travel at 100 to 400 linear feet per minute with the average speed of most machines of about 150 feet.

The porous chip absorbs moisture from the silicate forming a film on the surface of the paper. If the viscosity of the original silicate solution is too high, the film will have set by the time the liners come in contact with the chip. If the viscosity is too low, the silicate soaks into the chip without leaving an adhesive layer. The liners remove some additional water. This action together with an extremely slight amount of drying must set the silicate before the board is subjected to the stresses produced by the cutter. The time for this set is not over thirty seconds and with stationary cutters it is much less. Since different kinds of paper vary greatly in absorptive capacity, no definite figures can be set, but with $Na_2O:3.25SiO_2$ the useful range is between 160 and 775 centipoises.

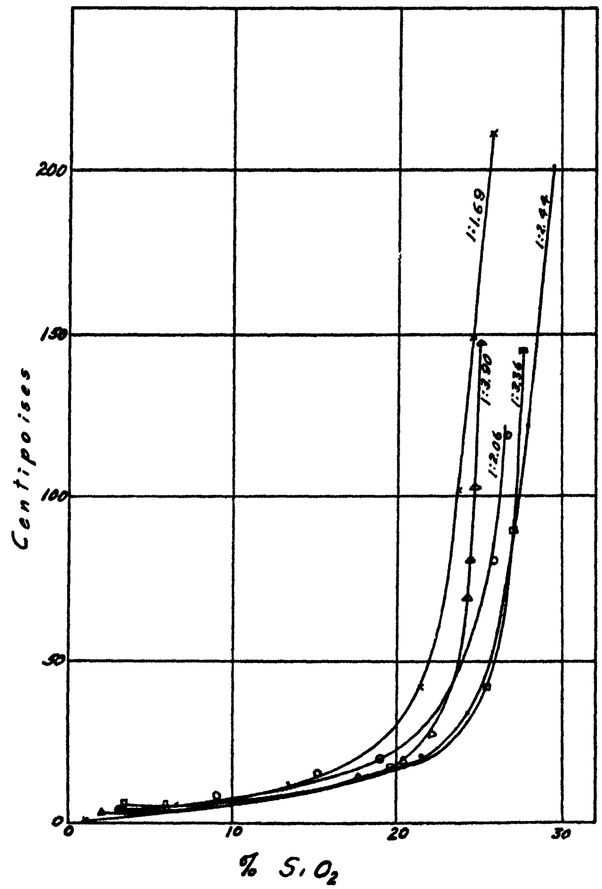

Fig. 3.

Solutions of the more silicious silicates may be used for this purpose. They, however, become increasingly difficult to handle under factory conditions because their viscosities change so greatly with temperature and with concentration. On the other hand, greater speeds are possible and boards with greater moisture resistance can be manufactured with these grades. The use of more alkaline silicates is limited by their tendency to saponify the rosin size. With very porous chip and non-absorbent liners the increased tackiness and wetting power resulting from the additional sodium oxide has been of value in some cases.

Fillers.

The properties of the adhesive solutions also can be modified by the addition of fillers. Mixtures with certain hydrous clays are not only much more viscous but also stickier. They set more slowly and will not spread as thinly as the silicate solutions alone. Such mixtures are used in the manufacture of wallboard. Whiting-silicate combinations are less tacky but seem to be especially good on dense hardwood surfaces.

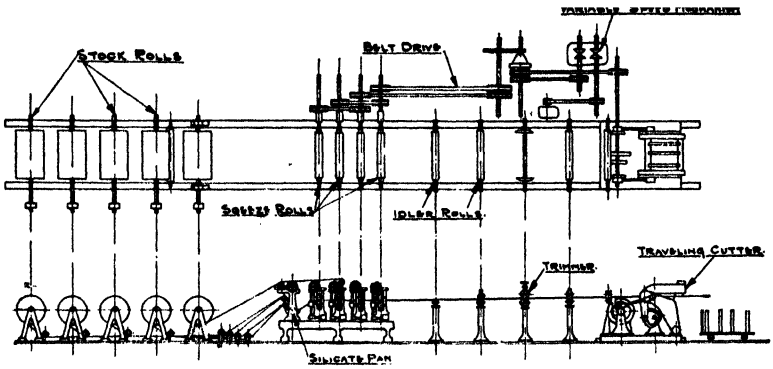

FIG. 4.

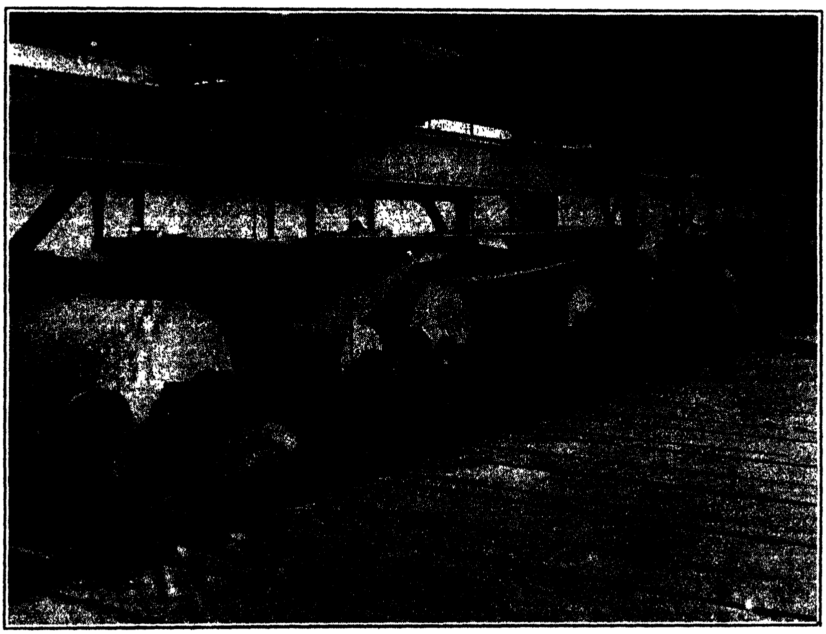

FIG. 5.

DEFLOCCULATION.

Sodium silicate solutions are not only of value in joining materials but also in separating them into very fine particles. This is illustrated by Fall's [2] work with manganese dioxide. Even when this material was ground in a colloid mill, very little of it could be suspended in water. If, however, 0.025 per cent of a solution of $Na_2O:1.6SiO_2$ were added, 4.52 and 3.48 grams per liter of the dioxide were deflocculated at 40° and 75° C., respectively. Other sodium silicates showed this ability also.

Clays are deflocculated whether they are mixed with small or large amounts of water. Thus about 0.1 per cent each of Na_2CO_3 and $Na_2O:3.3SiO_2$ will change a stiff, plastic filter cake containing 20 per cent water into fluid which can be pumped through a one-inch pipe. At the other extreme this same silicate will aid in the dispersion of clay used in paper stock. Here the total concentration of solids, including the pulp, does not exceed 2 per cent. Bleininger [3] found the effect varied with different clays but that in all cases silicate was more effective than other alkaline materials. Schurecht [4] found that 0.25 per cent $Na_2O:3.1SiO_2$ (based on the weight of the clay) gave the minimum viscosity with Georgia kaolin. At much higher concentrations the silicate ceased to be effective but the silicate had a longer effective range and gave a lower minimum viscosity than either caustic soda or sodium carbonate. Bodies made from the deflocculated clay were less porous and had greater dry densities and moduli of rupture.

Bleininger used $Na_2O:2.4SiO_2$ and Schurecht $Na_2O:3.1SiO_2$. McDowell [5] tried $Na_2O:1.8SiO_2$, $Na_2O:2.5SiO_2$, $Na_2O:3.3SiO_2$, $Na_2O:4.0SiO_2$, NaOH, Na_2CO_3, and a silica sol prepared by Bradfield's [6] method, with Florida kaolin. He found that the silicates were more effective, per unit of Na_2O, than either caustic or carbonate, but that the silica sol * was not a deflocculating agent at all. This was surprising because the most silicious silicate was better than the more alkaline ones.

Among the other materials deflocculated by sodium silicate solutions are quartz, phosphates, feldspars,[7] cumarone resins, mica, alkaline earth carbonates,[8] and barium sulfate.

The power of silicate to deflocculate clay is used by manufacturers of clay products formed by casting. The suspension of clay in water is not only easier to handle when deflocculated but a denser, stronger body results. When run into plaster molds, the clay is flocculated.[9] This process is used in the production of sanitary ware, porcelain table ware, and bricks. Even in electrical casting, deflocculation is necessary to obtain a dense deposit.

Washing Processes.

Not only clay but other silicious and non-silicious constituents of dirt are deflocculated by sodium silicate solutions. Since this action is one of the factors in washing processes,[10] sodium silicate solutions might be expected to act as detergents. This is actually the case, especially since they also have other detergent properties.[11] Recently Carter [12] has found that a soil or pigment may be deflocculated but still be taken up by the fabric. Even more startling is the discovery that soil may be removed from a dirty piece of cloth and concomitantly deposited on a clean cloth in the same wash liquor. Mixtures of soap and silicate are more effective than either one alone or than mixtures of soap and other materials commonly used as soap builders. This is particularly true in hard or softened waters.

Silicate Films.

There is some evidence that this protective action is largely due to the formation of a film on the surface of the textile fibers. In other ways silicate films are of value. In fact, if you say "silicate of soda" to most people, they look blank or else politely non-committal, but say "waterglass" and they usually say, "Oh, yes, for preserving eggs." For this purpose a 40° Baumé solution of $Na_2O:3.3SiO_2$ is diluted with ten to twelve parts of boiled water.

* Colloidal SiO_2 is a protective colloid. J. A.

The concentration should be adjusted so that the eggs will just sink. The dilute silicate solution reacts in the calcium compounds in the egg shell to form a film which, when wet, seals the egg. Only strictly fresh eggs can be kept in this way, since the film does not prevent further decomposition after it is once started. Fresh, sterile eggs were found to taste good after four years in the solution. Silicates as alkaline as $Na_2O:2.SiO_2$ have been used but are not recommended because they are liable to give the eggs an undesirable taste.

The interaction of calcium compounds with silicious sodium silicates is also used to harden and waterproof concrete surfaces.[13] This treatment may be applied after the concrete has been laid for three weeks or at any time thereafter until it disintegrates. An eight to ten per cent solution of $Na_2O:3.3SiO_2$ is usually used and applied three or more times with one-day intervals between applications. This is to insure maximum penetration and reaction. In addition to hardening and waterproofing the concrete, it is rendered oil- and acid-resistant. The exact reactions which take place between the hydrated Portland cement and the sodium silicate are not known. This is partly due to the complexity of the cement and partly to lack of knowledge about the silicate.

Chemical Reactions.

As a matter of fact, comparatively little is known about the chemical reactions of the sodium silicates in aqueous solution. The variable composition discourages investigators who prefer to start with a definite material. Even the work which has been done is full of contradictions, many of which are due to this factor. If results are reported without specifying the silicate, many questions remain. As an example of the possible contradictions the reaction with calcium carbonate studied by Carter[14] may be cited. He found that $Na_2O:2SiO_2$ would react with $CaCO_3$ but that neither $Na_2O:1.6SiO_2$ nor $Na_2O:3.3SiO_2$ showed any evidence of reacting within a period of a week. A further complication is introduced by the colloidal changes which take place at the same time as the chemical changes. By comparing the action of the corresponding sodium compound with the reacting material it may be possible to get some idea of which is which. This is a fertile field for investigation in the unexplored world of silicate chemistry.

Another method of eliminating or at least minimizing these disturbing colloidal effects is to allow the reactions to proceed at great dilutions. This method was used by H. T. S. Britton when he studied the precipitation of silicates by means of the hydrogen electrode.[15] The results he obtained are summarized in Table I and Figure 6. In this figure the arrows indicate the point of initial precipitation.[16]

TABLE I. *The Precipitation of Metallic Salts with 0.051 Molar Solution of $Na_2O:2.16\,SiO_2$.*

Solution Titrated	Precipitation Began At pH	With Cc. Silicate Soln. Added	Corresponding Hydroxide Pptd. at pH
0.01 *M* $ZrCl_4$	3.98	35.0	1.86
0.01 *M* $ThCl_4$	3.50	30.0	3.50
0.0067 *M* $Al_2(SO_4)_3$	4.04	5.0	4.14
0.02 *M* $BeSO_4$	5.31	20.0	5.69
0.02 *M* $ZnSO_4$	5.25	1.0	5.20
0.02 *M* $MnCl_2$	7.35	1.0	8.41
0.02 *M* $MgSO_4$	9.50	1.0	10.49
0.02 *M* $CaCl_2$	10.07	3.0	...

From a comparison of the pH values at which precipitation started with the salts and with the hydroxides, it would appear that the ion effect had been eliminated with thallium chloride and practically so with aluminum and zinc sulfates. These figures deal only with initial precipitation and not with the maximum, which Britton has shown [17] do not coincide, at least when solutions of the hydroxides are added to freshly made silicic acid. Thus the initial precipitation of calcium silicate started when the pH was 9.74 and the proportions were $CaO:5SiO_2$, but not all the silica was precipitated until the pH was 10.75 and ratio $CaO:3SiO_2$. Even then further changes took place when more hydroxide was added. Work in our laboratory has shown that the maximum precipitation from $Al_2(SO_4)_3$ and either $Na_2O:3.3SiO_2$ or $Na_2O:4.0SiO_2$ occurs when the pH is between 4.5 and 4.6 as compared with Britton's figure for the initial formation at 4.04.

Another interesting result of working at very low concentrations is that the reaction takes place with all the silica reacting as if it were a complex ion. This was recently shown in our laboratory in working with copper silicates. The sodium was replaced by an exact equivalent of copper and no excess of either copper or silica was left in solution. In more concentrated solutions, Jordis and Hennis [18] found that even an excess of copper would not precipitate all the silica. The study of other reactions at very low concentrations might help to bring order out of chaos.

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Porcelain and Allied Ceramic Bodies

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General Classification.

To define the heading "Porcelain and Allied Ceramic Bodies," it is probably best to consider Table 1 where a general classification of such products is given. While the chief constituents used are mainly the same and while the methods of manufacture and firing are in the main the same, the products may be quite different in appearance, porosity, thickness, and general properties. The term porcelain or china is usually confined to the products made non-porous by means of sufficient fluxes and firing. However, the term "porcelain" will here denote for brevity the general class of bodies being considered, which include earthenware, whiteware, semi-vitreous ware, china, porcelain for various domestic and technical purposes and the special porcelains.

"Porcelain" is a product obtained by intimately mixing the necessary ingredients obtained mainly by mining, shaping such mixtures and then firing the shapes. In American and European practice the common ingredients are feldspar, quartz or flint and clays. The feldspar and quartz may be mined and used as separate minerals, or they may be found intergrown and intermixed as in the English Cornish stone. Feldspar and quartz are also introduced as extraneous minerals found in the clays, sometimes to a rather large extent. The clays are of two general types—the ball clay which when wet gives the property of plasticity to the mixture, and the china clay which gives only slight plasticity. The two types of clays behave rather differently in the vitrification process.

Special porcelains are made by introducing other minerals and substances into the ordinary mixture and firing to appropriate temperatures. Such porcelain will be given separate consideration.

For an understanding of the properties of porcelain mixtures, it is essential to consider the properties of the individual raw materials and then to follow the changes in properties through the processes of intimate compounding, shaping, glazing and firing.

Table 1. *Porcelain and Allied Ceramic Bodies.*

Dishware (ornamental ware)	Low-medium fire	(1) Earthenware	Usually heavy and porous—not white	
" "	" "	(2) Whiteware	Both thick and thin sections; Usually white and porous	
" "	" "	(3) Semi-vitreous ware		
	Medium-high fire	(4) Porcelain-china	Usually thin—white non-porous	
Laboratory porcelain ware	High fire	Thin sections	Tubes, boats, dishes	non-porous usually white
		Thick sections	Ball mills, mortars	
Electrical porcelain	Medium-high fire	Thin sections	Low voltage	non-white porous usually white
		Thick sections	High voltage	
Special porcelains				

FELDSPARS.

The ceramic industry ordinarily employs what are commonly known as "potash" and "soda" feldspars, referring to the chief alkali present. Actually neither one of these feldspars is a pure mineral but usually a mixture of minerals of the feldspar family, orthoclase, microcline, albite and anorthite, with free quartz. The quartz is associated with feldspars either intergrown, where separation of the two minerals is difficult, or stratified, where separation of the two minerals is quite easily accomplished, by hand picking after coarse crushing. Cornish stone or china stone is a highly feldspathic granite which fuses white on firing. It is used in England as a source of feldspar, quartz being the chief remaining constituent.

For use, the feldspar rock is mined, crushed and ground to a fine powder, specifications being usually based on alkali content, silica content, fineness of material, fusion range.

Physical and Chemical Classifications of Ground Feldspar.

A conference held January, 1930, at the Bureau of Standards, Washington, agreed upon new classifications for ground feldspar used in "body mixtures," that is in mixtures as considered in this article. Tables 2, 3 and 4 give the Commercial Standard issued October, 1930.

TABLE 2. *Physical Classification.**

Mesh U.S. Standard Sieve Series No.	Percentage Remaining on 200 Mesh Screen	Maximum Percentage on Mesh Designated	Standard Screens—Openings in Inches U.S. Standard Sieve Series
230	0.00– 0.35	1.0	.0024
200	0.35– 1.00	1.0	.0029
170	1.00– 2.50	1.0	.0035
140	2.50– 5.00	1.0	.0041
120	5.00– 9.00	1.0	.0049
100	9.00–14.00	1.0	.0059
80	14.00–21.00	1.0	.0070
60	21.00–30.00	0.6	.0098
40	30.00–42.00	0.3	.0165
20	42.00–62.00	None	.0331

TABLE 3. *Chemical Classification.*

Group 1.

No.	Silica (SiO_2) Content, Per Cent
65	64.00-65.99
67	66.00-67.99
69	68.00-69.99
71	70.00-71.99
73	72.00-73.99

No.	Potash (K_2O)–Soda (Na_2O) Ratio
61	6 or more potash to 1 soda.
51	5 or more potash to 1 soda.
41	More than 3 and less than 5 potash to 1 soda.
31	3 or less potash to 1 soda.

* Based on fineness of grinding. Fineness classification shall be made on a basis of the percentage remaining on the standard 200 mesh sieve and that remaining on the sieve of the designated mesh. Example: 140 mesh product will have 2.5-5.0 per cent remaining on the 200 mesh sieve and less than 1 per cent on the 140 mesh sieve.

TABLE 4. *Theoretical Compositions of Pure Feldspar and Leucite.*

General Name	Potash Feldspar	Soda Feldspar	Lime Feldspar	
Minerals	Orthoclase Microcline	Albite	Anorthite	Leucite
Molecular Formula	1 K_2O 1 Al_2O_3 6 SiO_2	1 Na_2O 1 Al_2O_3 6 SiO_2	1 CaO 1 Al_2O_3 2 SiO_2	1 K_2O 1 Al_2O_3 4 SiO_2
Chemical Composition	Per Cent			
SiO_2	64.7	68.8	43.3	55.0
Al_2O_3	18.4	19.4	36.6	23.5
K_2O	16.9	—	—	21.5
Na_2O	—	11.8	—	—
CaO	—	—	20.1	—
	100.0	100.0	100.0	100.0

The Melting Behavior of the Feldspar Minerals.

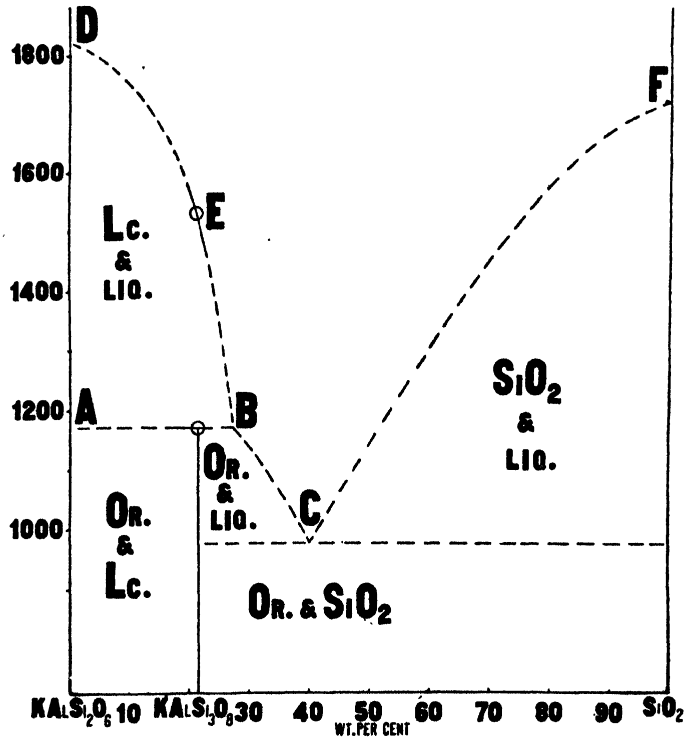
Orthoclase, Albite and Anorthite.—Albite and anorthite have definite melting points, being respectively 1,100° and 1,550° C.[18] These minerals are stable up to their melting points, and when the melting points are reached, the range through which softening occurs is relatively narrow as compared to orthoclase. Albite and anorthite form solid solutions between them, giving no eutectics but gradual melting and solidus curves from albite to anorthite.

Orthoclase (or microcline) is not stable at its melting point and hence forms part of a complex system. Morey and Bowen[17] have studied this problem and their results are given in the form of a melting point diagram between the substances leucite and silica (Fig. 1). Leucite has a high melting point, 1,686° C., and the crystals are isotropic or nearly isotropic, according to a new melting point determination made lately by Bowen and Schairer.[92] On the addition of silica to leucite, the melting point drops considerably until the eutectic *C* is reached around 980° C. The composition of orthoclase lies between these two points. On reaching a temperature of 1,170° C. orthoclase disintegrates, forming a new crystal phase, leucite, and a liquid. As the temperature is raised the leucite is taken into solution and the melting is complete at point *E*, corresponding to a temperature of 1,510° C. Hence for pure potash feldspar there is a wide softening and slumping range—from 1,170° to 1,510° C. The decomposition of orthoclase into leucite and glass may be written as

$$\underset{\textit{Orthoclase}}{K_2O.Al_2O_3.6SiO_2} = \underset{\textit{Leucite}}{K_2O.Al_2O_3.4SiO_2} + \text{glass}$$

The addition of free silica to orthoclase between compositions of orthoclase and point *B* should under equilibrium conditions give some liquid at 980° C., and at 1,170° C., the remaining orthoclase should break up into leucite and a liquid. Compositions between *B* and *C* should start melting at 980° C. and as the temperature is raised the orthoclase should go into solution, there being no formation of leucite crystals. The presence of more free silica beyond total compositions represented by *C*, will give a melting curve represented by *CF*, initial melting starting at the eutectic temperature 980° C.

In practice tetrahedral cones of the ground feldspar are made up usually bonded with organic substances, and the vitrification and slumping compared



Courtesy Amer. Jour. of Science.

FIG. 1.—Diagram illustrating the melting of leucite and silica.

with cones of known feldspars, pyrometric cones being present also for temperature check. The rate of firing is quite important as it affects the slumping range.

Solubility, in Melted Feldspar, of Quartz, Clay and Mixtures of Quartz and Clay.

Quartz.—Wetzel [48] determined the way in which the ground quartz rock or quartz sand went into solution when mixed with feldspar and fired. He found that the finer grains of quartz went into solution faster than the coarse grains. Norwegian potash feldspar dissolved more quartz than did the soda feldspar from Northern Bavaria. This statement is not verified by the work of Parmelee and Amberg,[50] who came to the conclusion that soda feldspar was a better solvent than potash feldspar for both quartz and clay. The solution of quartz in high soda feldspar *G* (Table 5) starts at about 1,350° C. and increases with temperature, 32 parts of quartz being soluble in 100 parts of feldspar by weight at 1,425° C. The solution of quartz in high-potash-feldspar *B* does not start until 1,400° C. is reached, and only 4 parts per 100 are soluble at 1,425° C.

Clay.—Parmelee and Amberg [50] determined also that the solution of clay in the high-soda-feldspar *G* started at 1,225° C. and at 1,425° C. 36 parts of clay per 100 of feldspar were taken into solution, whereas the solution of clay in the high-potash-feldspar *B* started at 1,250° C. and at 1,425° C. only 20.5 parts per 100 were taken into solution.

Quartz and Clay Mixtures.—Parmelee and Amberg [50] made porcelain mixtures of the composition china clay 30 per cent, ball clay 20 per cent, feldspar 30 per cent and quartz 20 per cent, fired them and determined the quantity of quartz removed by solution. At 1,425° C., it was found that the high-soda-feldspar *G* had taken into solution 60 parts of quartz per 100 parts of feldspar, when the clays were present. With the potash-soda-feldspar *C*, 50 parts of quartz had gone into solution with 100 parts of feldspar at 1,425° C. These results show the effect of the presence of clays upon the solubility of quartz in the feldspar, more quartz going into solution.

They report that in none of the mixtures of either feldspar and quartz or feldspar, quartz and clay was leucite to be observed in microscopic and X-ray diffraction studies. In this connection it should be borne in mind that the potash feldspar used by Parmelee and Amberg contained some soda which no doubt modifies the melting behavior of the orthoclase, and that the presence of silica in sufficient amounts prevents the formation of leucite, as shown in a previous discussion.

TABLE 5. *Composition of Feldspar.*

Type of Feldspar	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Feld-spar	Free Quartz
	Per Cent								
High-soda *G*	71.40	17.16	0.28	0.60	0.42	8.04	1.81	84.62	15.38
Potash-soda *C*	69.74	17.04	0.08	0.28	Tr.	3.29	9.09	85.55	14.45
High-potash *B*	65.58	19.54	...	0.16	0.20	2.56	12.44	100.00	....

SILICA MINERALS.

Quartz and Flint.

In the United States, potters' flint is the term applied to ground quartz, made by grinding quartz sand or quartz rock. In Europe flint used by potters is generally derived from flint pebbles. The flint pebbles are usually water-worn chert nodules. The pebbles are first strongly heated to cause them to lose their conchoidal fracture and toughness. After firing to about 1,300° C. the pebbles can be crushed and ground. In the heating process the colloidal organic matter to which is attributed the dark color of some pebbles disappears, leaving them gray to white in color. To a limited extent massive chert mined in Southern Illinois has been used in porcelain making.

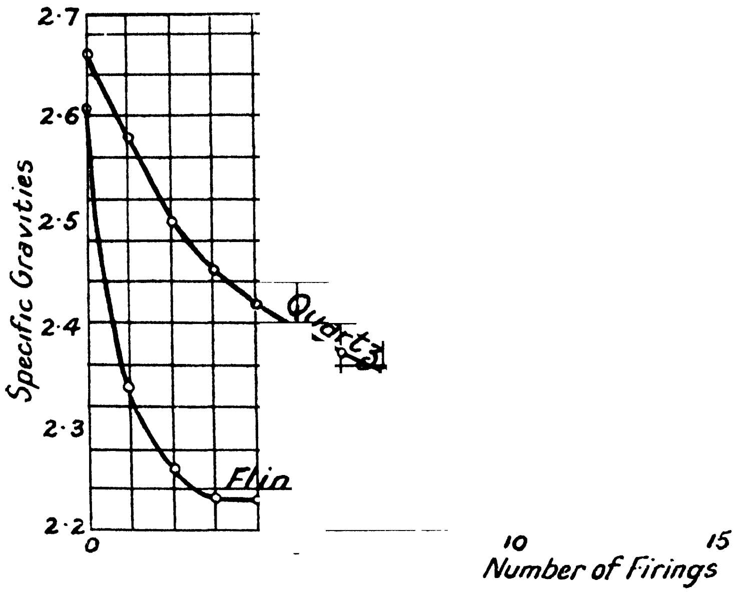
Quartz is a form of crystalline silica which under polarized light shows the usual properties of an optically uniaxial mineral with positive character. Flint and chalcedony, however, are found to have a fibrous structure, the crystalline fibers being woven together and only discernible under polarized light. As no actual individual crystals can be discerned, these minerals have been considered a colloidal form of quartz—there being other evidence to support this view.*

A typical chemical analysis of ground quartz for the manufacture of white-ware is SiO_2 99.60, $K_2O + Na_2O < 0.15$, $FeO + Fe_2O_3 < 0.05$, $CaO < 0.10$, $MgO < 0.10$, $Al_2O_3 < 0.10$ per cent.

* *See also* papers by C. Doelter and G. L. Clark in this volume.—J. A.

Effect of Heat on the Silica Minerals.

As heat affects quartz and true flint differently, these minerals do not act alike in a porcelain mixture, not only as mineral entities but also in conjunction with the fluxes which take the silica into solution.

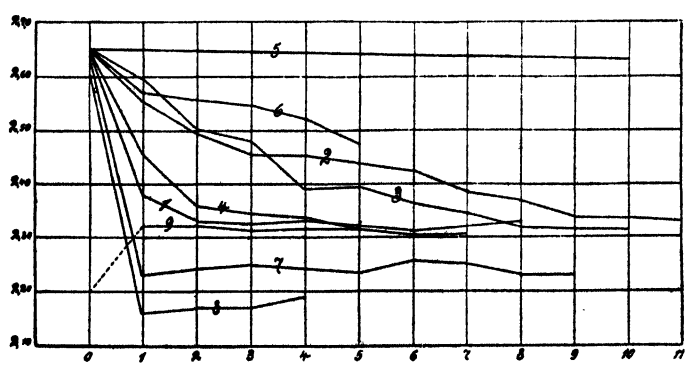


Courtesy J. Am. Ceramic Soc.

FIG. 2.—Effect of repeated firings on the specific gravity of flint and quartz.

Mellor and Campbell [15] showed the effect of repeated calcinations upon the specific gravity of flint and quartz (Fig. 2).

The flint reaches a lower specific gravity than quartz, and what is more



Courtesy J. Am. Ceramic Soc.

FIG. 3.

important the flint reaches the lower values with fewer firings. These inversions will be discussed later.

Rieke and Endell [94] made a somewhat similar study on a number of forms of silica and their data are given in their original form (Fig. 3).

TABLE 6. *Summary of Results.*[14]

Results in black face type were obtained in this investigation. After calcination at 1,450° C. for 2 hours the chalcedony analyzed 99.87 and the flint 99.6 per cent SiO_2. Inversion temperatures were obtained from cooling curves and volume changes with a dilatometer

	Raw Chalcedony	Raw Flint	Quartz		Calcined Chalcedony		Calcined Flint		Cristobalite		Tridymite		Silica Glass
			α	β	α	β	α	β	α	β	α	β_1	
Specific gravity, 25°/25°	2.55—2.61	2.61—2.63	2.65	...	**2.175**	...	**2.25**	...	**2.33**	...	**2.27**	...	2.194—2.213
Index of refraction	**1.533—1.538**	**1.533—1.539**	**1.544—1.553**	...	**1.456—1.470**	...	**1.483**	...	**1.484**	...	**1.475**	...	**1.457—1.460**
Inversion temperature, t_1			575°	570°	...	**220°**	...	**227°**	...	**244°**	**117°**	...	None
Coefficient of cubical expansion near t_1													
(*a*) Cc. per gram per degree × 10^4	...	...	0.25	—0.049	**1.3±0.3**	**1.4±0.2**	**0.9±0.4**	**1.4±0.3**	**1.1±0.5**	**1.5±0.4**	**0.15±0.12**	**0.38±0.08**	...
(*b*) Per cent per degree × 10^2	...	...	0.65	—0.12	**2.7±0.6**	**2.8±0.4**	**1.9±0.8**	**3.0±0.6**	**2.4±1.1**	**3.2±0.8**	**0.3±0.2**	**0.8±0.2**	...
(*c*) Ditto, from Braesco's data	...	...	...	...	...	...	...	...	1.6	0.65	0.53	1.0	...
Volume increase on inversion $\alpha \rightarrow \beta$ at t_1													
(*a*) Per cent	...	...	2.16		**2.63**		...		**2.83**		**0.142**		...
(*b*) Ditto, from Braesco's data	...	...	...		...		**3.09** ...		**2.4**		**0.2**		...
(*c*) Cc. per gram × 10^4	...	...	84		**131**		**150**		**132**		**6.3±0.6**		...

In general most of these silica minerals show a fairly sharp drop in specific gravity with repeated firing. It is noticeable how differently a substance acts when broken up to expose more surface, as for instance the rock crystal and gyserite.

A number of investigators have followed the effects of calcination on the silica minerals by other means than changes in specific gravity, as for instance by refractive index, volume increase at inversion points, coefficients of expansion and X-ray spectrographs. Some data are given in Table 6 and discussed briefly under the next heading of "Silica Minerals."

Silica Minerals.

Chalcedony, flint and quartz are found in nature fairly abundantly whereas the minerals cristobalite and tridymite are rather uncommon; they may, however, be prepared synthetically as was done by several investigators.

The stable ranges of the forms of silica with respect to temperature are shown in Figure 4, given by Fenner and reproduced with changes by Sosman.[6] Quartz is stable to a temperature of 870° C., tridymite is stable between 870° and 1,470° C., and cristobalite is stable between 1,470° and 1,710° C., liquid silica existing above 1,710° C. Conversion from one form to another is very sluggish.

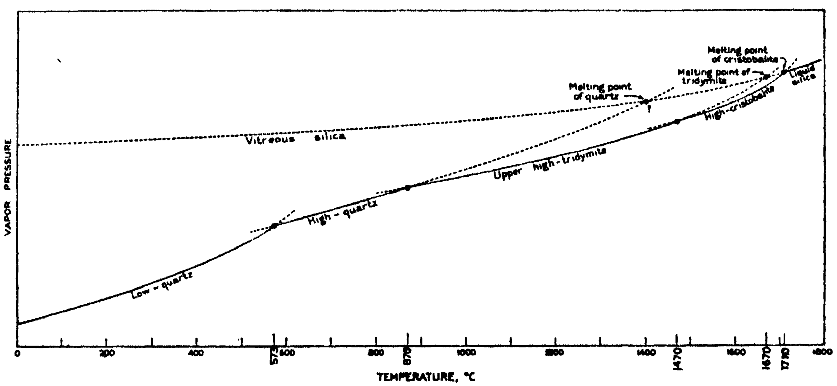


FIG. 4.—Stability ranges of different forms of silica.

Each of these crystalline forms has one or more inversion points at which the crystalline structure changes. These inversions occur rapidly and are reversible. Quartz inverts from the α to β form at 573° C., tridymite inverts from α to β_1 at 117° C. and from β_1 to β_2 at 163° C., and cristobalite inverts from the α to β form at some temperature between 200° and 275° C., depending upon the previous history of the sample. Sosman is advocating the use of the prefixes low- and high- for α and β and lower high- and upper high- for β_1 and β_2 as given above. Some of the quantitative data referring to these reversible inversions are given in Table 6. X-ray photographs show that the minerals flint and chalcedony are similar to quartz in their crystal structure, the difference in optical properties and physical behavior being attributed to the colloidal nature of the flint and chalcedony.

The X-ray photographs show also that calcining the flint and chalcedony causes these minerals to assume a crystal structure similar to the structure of cristobalite. Quartz is converted to cristobalite under the same heat treat-

ment, hence it may be stated that for all intents and purposes calcined flint and calcined chalcedony are similar to cristobalite. While there are variations in specific gravity and in refractive index there is a general similarity in the large volume change at the α to β inversion and in the coefficient of expansion for these three substances.

The crystal structure of tridymite as noted from the X-ray spectra differs greatly from the other silica minerals and from the ordinary calcined products.

The Effect of Prolonged Grinding on the Density of Quartz.

As quartz rock is ground quite fine for whiteware bodies the effect of long grinding is of interest in this discussion.

Johnston and Adams [48] determined the densities of quartz powder of different degrees of fineness and came to the conclusion that "When homogeneous material, free from cracks and holes, is powdered, the change of density thereby produced is but little greater than the error of the method employed. It may be noted, however, that the change, if real, is . . . a decrease. . . ."

Ray [19] considered the decrease in density of 4.17 per cent obtained by grinding quartz for 15 hours to be due to the conversion to silica glass (a 25.7 per cent conversion).

Dale [20] repeated the experiment grinding for 6 hours in an agate mortar, and allowing for contamination from the mortar, obtained a slight decrease in density equivalent to a conversion to silica glass of only 1.9 to 2.6 per cent.

Martin and Watson [21] starting with quartz sand of density 2.650 found after grinding 25 to 50 minutes a density of 2.653 and after 3½ hours a density of 2.649 equivalent to a conversion to amorphous silica of 0.91 per cent. These results agree with Dale's quite well.

Making due allowance for impurities obtained from the grinding media, there is evidence enough that the density of quartz is slightly lowered on long grinding. No definite evidence has been presented, however, to support the claim that the constituent of lower density is silica glass or amorphous silica.

Researches on the Theory of Fine Grinding.

Mention should be made of the fine work performed by Geoffrey Martin [49] and a group of co-workers on the "Theory of Fine Grinding" using crushed sand (quartz) for their material, the work extending over a period of at least six years. The subjects of the papers reported in the Transactions of the (English) Ceramic Society show the extent of the investigation.

Part I. "Law governing the connection between the number of particles and their diameter in grinding crushed sand," by Geoffrey Martin, Charles Blythe, and Harold Tongue, **23**, Part II, p. 61 (1923-24).

Part II. "A method of accurately determining experimentally the surface of crushed sand particles," by Geoffrey Martin, Edgar A. Bowes, and J. W. Christelow, **25**, Part I, p. 51 (1925-26).

Part III. "Connection between the surface area produced and the work done in a tube-mill grinding of quartz sand," by Geoffrey Martin, Edgar A. Bowes, and F. Brand Turner, **25**, Part I, p. 63 (1925-26).

Part IV. "On the air analysis of large quantities of crushed sand," by Geoffrey Martin and Walter Watson, **25**, Part III, p. 226 (1925-26).

Part V. "On the existence and preparation of statistically homogeneous grades of crushed sand," by Geoffrey Martin, Ernest H. Coleman, Edgar A. Bowes, and T. H. Littlewood, **25**, Part III, p. 240 (1925-26).

Part VI. "On the diameter of irregularly shaped sand particles sifted by air currents of different speeds and different temperatures," by Geoffrey Martin, **26**, Part I, p. 21 (1926-27).

Part VII. "On the efficiency of grinding machines and grinding media with special reference to ball and tube mills," by Geoffrey Martin, assisted by F. Brand Turner and Francis Linstead, **26**, Part I, p. 34 (1926-27).

Part VIII. "On the variation in the specific gravity of quartz sands on prolonged grinding," by Geoffrey Martin, assisted by Walter Watson and Edgar Bowes, **26**, Part I, p. 45 (1926-27).
Part IX. "Connection between the statistical diameter and the statistical volume of irregularly shaped particles of crushed sand," by Geoffrey Martin and Edgar A. Bowes, **27**, Part IV, p. 247 (1927-28).
Part X. "On the connection between the statistical diameter of crushed sand particles and their statistical surface," by Geoffrey Martin and Edgar A. Bowes, **27**, Part IV, p. 259 (1927-28).
Part XI. "Calculations relating to diameters, surfaces and weights of homogeneous grades of crushed quartz sand," by Geoffrey Martin, **27**, Part IV, p. 285 (1927-28).

Clays.

Properties.

Bleininger [5] has given an excellent definition of a clay by stating "Clays are soft or consolidated rocks consisting essentially of hydrous silicates of alumina of the type Al_2O_3, $2SiO_2$, $2H_2O$, which when admixed with water, are capable of being molded under a *low* pressure and which retain the shape imparted upon removal of the pressure. Furthermore, the clays harden upon the application of heat and finally form a rock-like mass of varying degrees of porosity." Only two types of clays—the china clay (or kaolin) and ball clay—are used in the making of "porcelain," although there are many types of clays mined and used for other purposes.

Clays

China clay or kaolin * is the product of the disintegration of granite and feldspars, the process being known as kaolinization. Pegmatite rock on weathering completely, yields kaolin in place of the original feldspar; the quartz and mica (muscovite) remaining as impurities. Examples [1] are to be found in the North and South Carolinas.

True china clays or kaolins are residual or primary clays—that is, they are found in the same location as the parent rock whose disintegration formed them. These clays are usually associated with quartz (and mica), and it is necessary to put them through an extensive washing process before they are ready for use.

In the washing process, the large sand or quartz grains are allowed to settle first, and then the mica and fine sand are removed in succeeding settling operations. The suspension contains usually 10 to 15 per cent clay substance.

Where the clay banks are washed down it is a common practice [9] to add acid to the water to coagulate the clay particles. Again when it is desired to maintain the finer particle of clay in suspension, an alkali like sodium silicate is added (*see* "Effect of Electrolytes").

The whiteware industry makes use also of transported or *sedimentary clays,* which, when white burning, are known as kaolins or plastic kaolins.[1] Such clays are to be found in Georgia, South Carolina and Florida. The transported clay deposits are formed by the residual clays which are washed away and deposited and form stratified sedimentary clays.[2]

By *ball clay* is meant the plastic clays used in the industry. In the whiteware mixtures, only white-burning ball clays are used.

Ball clays are of sedimentary character, that is, they have been transported from their place of origin (as residual clays) and laid down again in lower regions. Ball clays are mined in large balls or masses about 1 cubic foot in volume and shipped in this condition. The ball clays are quite dark in color,

* The name is derived from a Chinese mountain Kao Ling, where China clay was obtained.—J. A.

some being almost black. The color is due mainly to organic matter in all states of subdivision.

In England, ball clay comes from Dorsetshire and Devonshire. In the United States, Florida, Kentucky, Tennessee and New Jersey have deposits of ball clay.

Microscopic Examination of Clays.

Somers[51] called attention to the fact that clays contained distinctly micaceous minerals besides those of kaolinite. From microscopic studies of the optical properties of the minerals contained in clays, he came to the conclusion that there was an isomorphous gradation from sericite (the muscovite mica) to kaolinite (the clay substance), by means of a gradual loss of potash and by an addition of water of crystallization. The weathering of these intermediate compounds yields the hydromicas, which constitute the micaceous minerals found in clays. These changes may be represented:

Sericite (Muscovite Mica).	$K_2O.3Al_2O_3.6SiO_2.2H_2O$
$\downarrow$	$\downarrow$
Hydromica	Isomorphous gradation between Sericite and Kaolinite
$\downarrow$	$\downarrow$
Kaolinite	$3Al_2O_3.6SiO_2.6H_2O$ or $(Al_2O_3.2SiO_2.2H_2O)$

A distinction was made by Schurecht[40] in his microscopic examination of china clays and kaolins between coarse-grained clays and fine-grained clays (he used the terms crystalline plates and colloidal aggregates). The coarse-grained clays were made up of crystalline plate-like grains, whereas the fine-grained clays were mainly aggregates of very fine particles. The English china clays and North Carolina kaolins belong to the coarse-grained type whereas the Georgia white clays and the South Carolina white clays belong to the fine-grained type. It is suggested that the better drying properties of the coarse-grained clays are due to the fact that the water can pass through the interstices and capillaries uniformly and readily and with less drying strains than through the fine-grained clays.

From a microscopic examination of some 250 secondary French clays Bertrand[41] concluded that the alkalies were present as material adsorbed by the colloidal clay, thus refuting in a way the suggestion of Somers that there were present hydrated alkali aluminum silicates. The clay base was composed of colloids and crystalline kaolinite, as well as cryptocrystalline material especially abundant in halloysite.

Ross and Foshag[62] have determined that the usual so-called kaolins contain to quite a large extent a mineral known as "anauxite." Its chemical analysis indicates a formula of $Al_2O_3.3SiO_2.2H_2O$. For some time it was assumed that the mineral "kaolinite" with formula $Al_2O_3.2SiO_2.2H_2O$ was the chief constituent of clays. By petrographic and X-ray analyses Ross and Kerr[74] have found and described two more minerals which belong to the kaolin family. These clay minerals are "nacrite" and "dickite," and they can be distinguished from "kaolinite," although the chemical composition is the same for all three. Kaolinite still remains the characteristic clay mineral of commercial china clays and kaolins.

Ultramicroscopic Examination of Clays.

An ultramicroscopic examination of some clays by Alexander [52] revealed rather marked differences in clays, and these differences were correlated with some known properties of the clays. The clays were mixed with water, well stirred and then observed, no attempt being made to add deflocculating agents. The clays were examined for large particles—average diameter 0.025 mm., small particles, 0.005 mm., and colloidal particles of submicroscopic size. One great difference between primary and secondary clays was the presence of large particles in the primary clays, and their absence in the secondary clays. The kaolins showed rather active colloidal motion, whereas the ball clays showed rather slow or hampered colloidal motion which generally accompanied the coagulated clays, due to the presence of flocculating substances. The kaolins were thus rather free of iron salts, chlorides, sulfates and acids which act as coagulants. The clays examined included English, Georgia, Florida and North Carolina kaolins, and Tennessee and Kentucky ball clays. A Delaware kaolin known to be a primary kaolin showed all the characteristics of a secondary clay, namely large reticulated gel groups, hampered colloidal motion and the presence of coagulants.

France [42] took ultramicroscopic motion pictures of clays, with the view of correlating their colloidal content and plasticity. He considered that the colloidal state of matter lies within the limits of 0.1 μ and 1 mμ,

$$(\text{where } 1\ \mu = \frac{1}{1000}\ \text{mm. and } 1\ \text{m}\mu = \frac{1}{1{,}000{,}000}\ \text{mm.})$$

$$\text{where}\begin{cases} 1\ \mu = \dfrac{1}{1{,}000{,}000}\ \text{m.} \\ \text{and } 1\ \text{m}\mu = \dfrac{1}{1{,}000{,}000}\ \text{mm.} \end{cases}$$

Assuming that as the colloid content of a clay increased the plasticity increased, he endeavored to list the clays by means of their colloidal content, and suggested for increasing plasticity the order, North Carolina, South Carolina, English China clays.

Testing Clays for Suitability.

A recent publication of test methods and results obtained by Parmelee and McVay [28] on 13 ball clays and 7 China clays and sedimentary kaolin used in the manufacture of electrical porcelain gives an excellent survey of the kinds of tests used in the ceramic industry for this purpose. The methods described below are given in outline only, and the results in summary form—Table 7.

Tests made on the Raw Clays in Water-Suspension.

1. Deflocculation Test—The clay is mixed with water and varying amounts of electrolytes, and the suspensions are held in tall containers, the amount of settling being noted.
2. Malachite Green Absorption Test—Definite amounts of clay are added to the dye in solution. The removal of dye from solution by the clay is determined colorimetrically.

Tests made on the Unfired Specimens Shaped from Plastic Masses.

The clay is tempered with water and thoroughly worked to a plastic condition. Shapes are pressed in molds using the plastic mass.

3. Water of Plasticity—The amount of water required to give a clay this plastic condition is determined by noting the loss in weight by drying at 110° C. and is calculated as a percentage of the dry weight of clay.

4. Volume Shrinkage on Drying—The plastic specimen bars made by molding are weighed, and their volumes measured by one of several methods—pycnometer or overflow volumeter using kerosene as the liquid. After drying at 110° C., the specimens are weighed in air and in kerosene (after a soaking period) to determine volume and specific gravity.
5. Transverse Strength Tests—Specimen bars are made either of the clay alone or with potter's flint in equal weights, dried and then broken in transverse, the modulus of rupture being calculated.

Tests made on Fired Specimens.

6. Oxidation Behavior—Specimens of thick cross-section are fired to 700° C. and held for 5 hours at that temperature. The specimens are then broken and the relative (dark) areas of incompletely oxidized material noted.
7. Volume Firing Shrinkage—Specimen bars are fired to various temperatures either in separate burns or in a single burn, draw trials being taken at the required temperatures. The shrinkage in volume due to firing may be determined by a density determination, or by calculation from the linear contraction obtained by noting the change in length of a specimen or of a distance between scratches on a specimen.
8. Specific Gravity (three forms)—Bulk specific gravity is the weight per unit of exterior volume.

   Apparent specific gravity is the weight per unit of volume of water-impermeable portion. This is obtained by soaking the specimen for a long period of time and weighing in water.

   True specific gravity is the weight per volume of the solid material ground fine enough to obliterate sealed pores and water-permeable pores. A pycnometer is usually employed for this test.

TABLE 7. *Testing of Clays.*

	Thirteen Ball Clays (washed and crude)	Seven China Clays Kaolins (washed)
Water of plasticity (per cent)	30.3 –54.8	33.5 –39.7
Volume drying shrinkage (per cent)	18.3 –35.7	13.3 –23.6
Bulk density of dried clay	1.49– 1.92	1.45– 1.59
Modulus of rupture of 1:1 clay-flint mixture (lbs. per sq. in.)	284–819	134–335
Malachite green adsorbed per gram of clay	.045–.059	.015–.045
Volume firing shrinkage (per cent)		
Cone 6	13.3–39.6	17.7–33.7
10	15.2–42.3	23.0–38.7
14	8.7–48.0	33.8–49.0
Apparent porosity (per cent)		
Cone 6	0.2–28.4	29.2–39.7
10	0.0–37.7	22.3–36.2
14	0.1–35.3	3.2–24.5
Total per cent porosity based on bulk volume		
Cone 6	2.3–30.4	30.3–42.0
10	2.5–27.3	25.7–39.4
14	2.1–20.3	8.7–29.9
Bulk specific gravities		
Cone 6	1.88–2.51	1.54–1.90
10	1.93–2.48	1.65–2.03
14	1.92–2.59	1.91–2.45
True specific gravities		
Cone 6	2.466–2.709	2.693–2.722
10	2.456–2.689	2.710–2.744
14	2.405–2.650	2.712–2.740
Apparent specific gravities		
Cone 6	2.12–2.68	2.47–2.67
10	2.05–2.63	2.49–2.63
14	1.95–2.62	2.45–2.60
Closed pores (per cent)		
Cone 6	1.2–13.5	1.8–8.6
10	1.6–18.3	4.2–8.0
14	0.9–18.0	5.0–9.3

9. Porosity—Weighing a specimen dry and then after a soaking in water, gives an increase in weight, which is a measure of the open and connected pores in the piece. This pore volume can also be determined directly by means of a porosimeter which measures the volume of gas or air held in the connected pores.
   From the bulk specific gravity and the true specific gravity, the volume of the total pores (open pores and closed pores) can be calculated.
10. Color of Fired Clay—For whiteware it is highly desirable that the clays fire to a white or approximate white color with slight or no amounts of staining. In general the kaolins fire whiter than the ball clays. The atmospheric conditions of the kiln and the rate of firing have a bearing upon the results, oxidizing conditions giving on the whole the better conditions.

Plasticity.

Jenks [67] believes that "the cause of plasticity of clay is the formation in the moistened clay of a continuous external phase through the action of water in making gelatinous the material that forms the enveloping surface around the non-gelatinous particles and aggregates present in the clay." . . . "The presence of organic matter, of dissolved carbon dioxide, or of electrolytes in the water or in the clay itself is not the cause of plasticity of clay. Such materials are agents through the action of which a sufficient amount of material, capable of becoming gelatinous when moistened, is formed and, once having been formed by any agent, is maintained." . . .

Plasticity and Algae Growth in Clay Masses.—Aging of clay and clay-containing masses in the plastic form has been resorted to quite frequently to develop and increase the property of workability. Spurrier [83] has found that the storage of wet clay involved the growth of algae, and that the increase in plasticity was a result, in part at least, of the algae growth. Of four varieties of algae found in the clay, the green algae or "chlorophyceae" were the most common. For the flourishing of the algae fresh oxygen and moisture were necessary, both being found in the plastic clay.

The metabolism of the algae involves the formation of gases—carbon dioxide and carbon monoxide, such gases being absorbed in the plastic clay mass and, according to Spurrier, causing a reduction in plasticity. Churning a plastic clay mass in a poorly designed pug-mill will mix in air and cause the mass to become "short," i.e., lose some of its plasticity, hence it is common factory practice to have well-designed pug-mills in use. In order to remove these gases of metabolism Spurrier has developed an evacuation scheme which consists of evacuating the plastic mass to as high a vacuum as is obtainable with moisture present, and then breaking the vacuum with extreme suddenness, causing the collapse of the mass. The evacuated mass shows greater plasticity than the unevacuated body.*

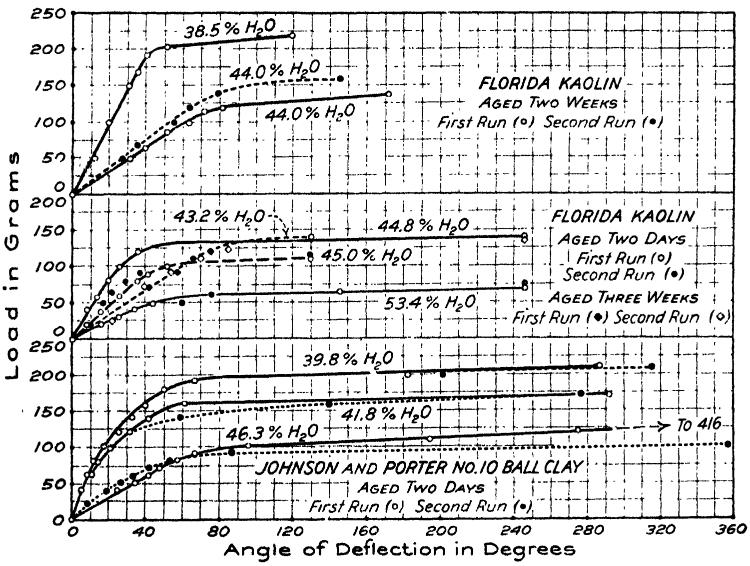
Direct measurement shows that the alumina soluble in dilute alkali contained in a clay slip is increased by the growth of algae, and the greater the growth the more soluble alumina there is present. Adding one-half per cent of hydrogel of alumina to a clay body of poor plasticity increases the plasticity to a marked degree, and represents an inorganic change corresponding to the change made by the algae in breaking down the clay.

Measurement of Plasticity.—A number of attempts have been made to measure the property of plasticity, so important in ceramic processes. Plasticity has been measured by determining the deformation caused by stress applied in compression, in tension and in torsion. Talwalkar and Parmelee [68] and Parmelee and Rudd,[69] latest workers in this field, have preferred to apply the stress in torsion. Irving and Dietrich [70] have adopted their method for some investigative work. A test piece of plastic material is shaped in the

* This seems to be an interesting instance of a gas-in-solid dispersion.—J. A.

form of a cylindrical bar 4″ long and 1″ diameter with square shaped ends. The two ends are held in square shaped chucks, only one being free to move in a rotary manner. A load is applied by means of a pulley attached to the movable end. The torsion in degrees is measured on a scale and determined for each weight applied. A stress-strain diagram can thus be plotted as shown in Figure 5.

There are two slopes to each curve, the second slope being much flatter, indicating a much greater rate of deformation. The greater the stress attainable, the greater is the ability of the mass to withstand deformation. The longer the second (or flat) part of the curve, the more deformation will the mass withstand without rupture. Data are rather few and, in general, simple mixtures with fairly high water content have been examined.



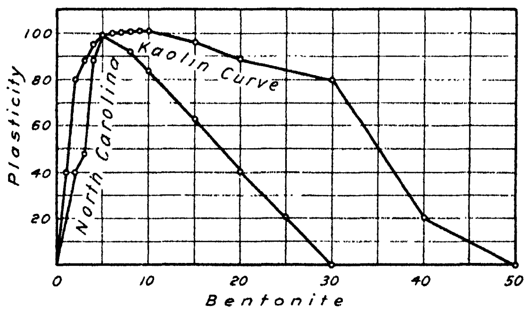
Courtesy J. Am. Ceramic Soc.

FIG. 5.—Torsion data obtained on different clays.

Irving and Dietrich have given some tentative generalizations which are worth mentioning: (*a*) The plastic torsional strength of a clay probably varies directly with the water content. (*b*) The total deformation below rupture tends to increase with increase in the water content. (*c*) Ageing of clay in the plastic condition decreases the plastic torsional strength and tends to increase the total deformation before rupture; for a given strength, ageing permits the use of less water without lowering the total deformation. (*d*) Progressive additions of finely ground quartz up to 50 per cent have a tendency to increase the plastic torsional strength and to decrease the deformability of clays; beyond 50 per cent the plastic strength is rapidly decreased by increase of quartz, but the deformability is very slightly affected. (*e*) The plastic torsional strength of a mixture of equal parts of clay and non-plastic matter may be increased by increase in fineness of the non-plastic portion. (*f*) No correlation was obtained between the adsorption of malachite green and of methylene blue by various clays. No correlation was obtained between

the amounts of either dye adsorbed and the plasticity or other properties of clay.

Plastic Clay Masses Obtained by Addition of Bentonite.—Cox [84] caused a North Carolina kaolin and a calcined Florida clay to become as plastic and workable on a potter's wheel as a Kentucky ball clay, by the addition of bentonite. The criterion was the ability of the plastic mass to be worked into thin shapes without splitting in the process. Thin ware was fired also. The graph (Fig. 6) shows the calculated plasticity plotted against the percentage additions of bentonite. It should be noted that the high plasticity is obtained only with certain additions of bentonite, 5 to 15 per cent, according to the clay,



Courtesy J. Am. Ceramic Soc.

FIG. 6.—Effect of addition of bentonite to clay.

and that the plasticity is assumed to be due to the addition of the colloid minerals contained in bentonite.

Bentonite.—Ross and Shannon [75] have examined a large number of bentonites and have come to some interesting conclusions regarding this clay material. Bentonite is a clay material resulting from the devitrification and chemical alteration of volcanic glass. The alteration products are minerals—the most common mineral is "montmorillonite," $(Mg,Ca)O.Al_2O_3.5SiO_2.5\text{-}8H_2O$, a less common mineral is "beidellite" $Al_2O_3.3SiO_2.4H_2O$, and a still less common mineral—"halloysite" $Al_2O_3.2SiO_2.3\text{-}5H_2O$. These minerals are completely crystalline and, on account of their micaceous habit and cleavage, present a large amount of surface. Bentonite contains no gel colloids, but swells to varying degrees and crumbles in water. It is maintained that bentonite is an example of a crystalline dispersoid and owes its high adsorption efficiency to its plate-like structure and permeable texture.

HYDROGEN-ION CONCENTRATION OF CLAY-WATER SUSPENSIONS.

Water suspensions of clays usually yield pH values on the acid side, namely below 7. Thus Hall [11] found 10 kaolins and China clays to have an average of 5.3, the values ranging between 4.4 and 6.8, and found 21 ball clays to have an average of 4.7, with values between 3.2 and 6.0. These measurements were made on suspensions containing 20 per cent clay. On the average the ball clay suspensions are found to be more acid than the kaolins and China clays.

The soil chemists have been very much interested in the cause for the acidity of clays in suspension. Bradfield [4] centrifuged a soil in water, and obtained clay particles of less than 1 μ in diameter which he thought constituted a true colloidal acid. Salter and Morgan,[10] however, believed that

the acidity was due to a preferential adsorption of the OH ion by the soil colloids.

The clay particles in a water suspension are found to be charged negatively, and proceed towards the anode in an electrical field. Use is made of this property in several ways where it is desirable to concentrate the clay particles from a water suspension.

Effect of Hydrogen-ion Concentration on Properties of Suspensions.

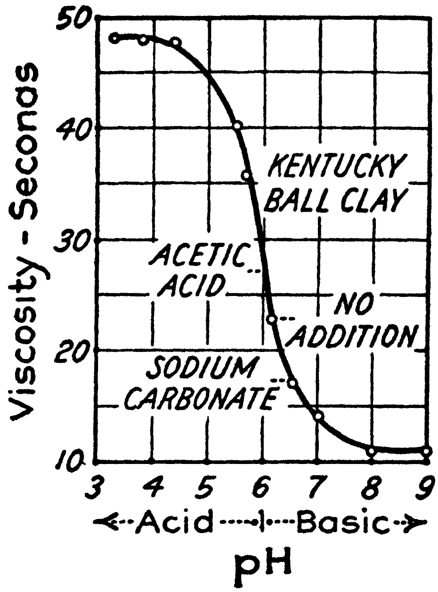
(1) *Viscosity.*

Additions of a basic electrolyte like sodium carbonate or sodium silicate to a clay slip (a water suspension) usually causes a lowering of the viscosity, reaching a minimum and then increasing slightly. The viscosity is measured by timing the flow of a given volume of slip through an orifice. Examples of such curves are given in Figures 13 and 14.

Randolph and Donnenwirth [22] have taken the viscosities of a Kentucky ball clay slip over a wide range of H-ion concentration and obtained an interesting curve (Fig. 7). The viscosity of the slip on the acid side is quite high in comparison with the viscosity on the alkaline side.

Clays are sometimes obtained which do not act towards electrolyes in the ordinary manner. The writer had occasion to experiment with a Canadian ball clay which was rather alkaline in a water suspension as compared with other ball clays:

	pH
Canadian ball clay	8.0
Ivory fat ball clay...........	6.7
Tennessee ball clay..........	6.1
Kentucky ball clay	5.6



Courtesy J. Am. Ceramic Soc.

FIG. 7.—Effect on viscosity of addition of acid and alkali to ball clay.

In order to deflocculate this clay it was necessary to add an acid. The viscosity curve (Fig. 8) is given to show the changes occurring.

This case serves to show that clays as mined may be radically different in their state of aggregation due to the presence of salts and absorbed ions obtained from their environment. It is desirable and in fact necessary to treat experimentally each clay by itself and determine the best working conditions for it.

(2) *Flocculation.*

As the pH of a clay-water suspension is changed by means of electrolytes, the colloidal condition of the suspension can be seen by the changes occurring in the aggregation of the clay particles. Hall [11] showed that at a high acidity corresponding to a pH of 2.7 to 4.0 ball clays and China clays show a maximum rate of settling (Fig. 9). This narrow range corresponds to the iso-

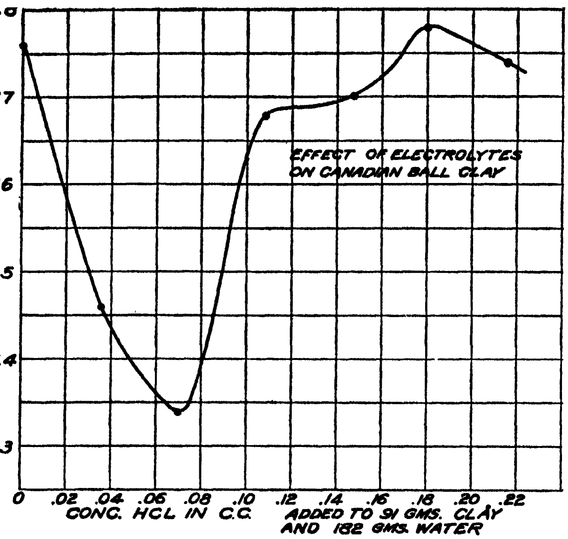
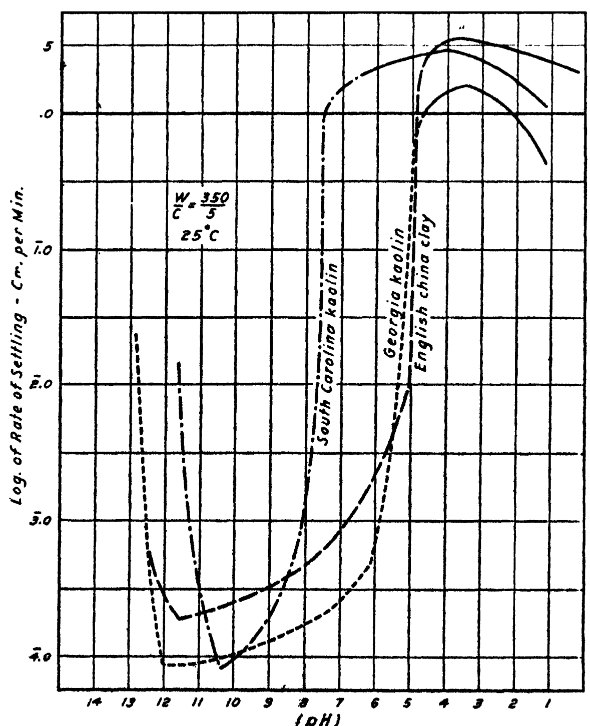


FIG. 8.—This case serves to show that clays as mined may be radically different in their state of aggregation due to the presence of salts and absorbed ions obtained from their environment. It is desirable and in fact necessary to treat experimentally each clay by itself and determine the best working conditions for it.



Courtesy J. Am. Ceramic Soc.

FIG. 9.—Showing the relation between the rate of settling of three kaolins and the pH value of the suspending medium. The full lines indicate the average rate of settling of the flocculated clay and the broken lines indicate the rate of settling of the finest particles over the deflocculated range.

electric point, that of maximum flocculation. On causing the suspension to become alkaline, a point is reached between pH 11 and 12 where the settling is at a minimum, corresponding to the maximum degree of deflocculation. Neither of these points is very sharp, depending upon the water-clay ratio of the suspension, and upon the presence in the clay of other colloids, as silica and alumina.

At the iso-electric point the electric charge on the clay particle may be considered zero, and the addition of an acid will give a positive charge to the particle, whereas the addition of an alkali will give a negative charge to the particle. (The addition of an acid decreases the pH of the suspension, and the addition of an alkali increases the OH-ion concentration.) The amount of negative charge can be increased to a maximum corresponding to the point of maximum deflocculation, and the further addition of alkali then causes a decrease in the negative charge carried by the clay particle.

(3) *Effect of Mixing Two Clay-Water Suspensions.*

Bleininger [24] showed the effect on viscosity of mixing clay suspensions in a porcelain body mixture. A composition of feldspar 21 per cent, quartz 34

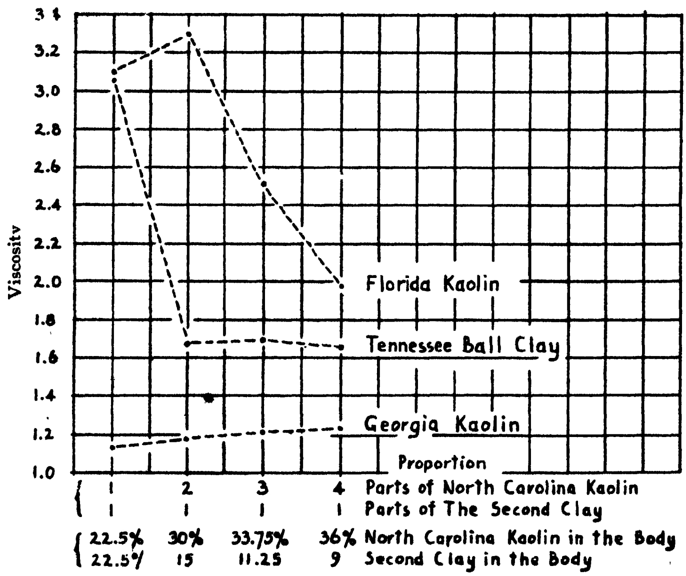


FIG. 10.

per cent and clays 45 per cent was maintained. North Carolina kaolin was present in each of a series of mixtures to which was added another clay to maintain the total clay content of 45 per cent as follows:

	Per Cent			
North Carolina Kaolin	22.5	30	33.8	36
A Second Clay	22.5	15	11.2	9
Total	45	45	45	45
Ratio of $\frac{\text{North Carolina Kaolin}}{\text{A Second Clay}}$	$\frac{1}{1}$	$\frac{2}{1}$	$\frac{3}{1}$	$\frac{4}{1}$

The second clay was either Georgia kaolin, Florida kaolin or Tennessee ball clay. Viscosities of the suspensions were made and the results are plotted (Fig. 10), the curves being labeled with the clay substituted for the North Carolina kaolin in the mixture. The three clays act very differently under these circumstances. Increase in the Georgia kaolin content causes a slight lowering in the viscosity, signifying a deflocculating action. Adding the Tennessee ball clay causes slight increase in viscosity up to 15 per cent, and the further addition causes a very marked increase in viscosity and in flocculation. The increase of Florida kaolin content causes the viscosity to rise to a maximum, after which it falls slightly. The three curves are entirely different representing different behaviors.

(4) *Plasticity.*

For a Kentucky ball clay suspension Randolph and Donnenwirth [22] show the effect of the pH on the plasticity measured according to Bingham's method.

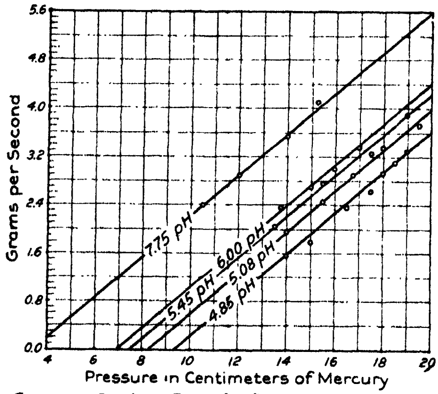


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FIG. 11.—Effect of pH on plasticity of Kentucky ball clay (old mine No. 4).

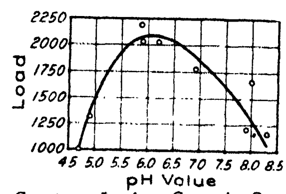

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FIG. 12.—Effect of pH on dry strength of spark plug body.

It is seen that the slope for the different pH values is the same, indicating that the "mobility" or rate of flow is the same. However, the "yield value" or stress required to start the flow is greater for the low pH (acid) values where the clay is flocculated than for the higher (more alkaline) pH values where the clay is less flocculated.

(5) *Dry Strength of a Body.*

Several investigations have shown that the strength of a "porcelain" body can be varied depending upon the pH of the slip from which the body was made. Bleininger [24] gives some data, and Randolph and Donnenwirth [22] give a curve (Fig. 12) which is very enlightening, showing that the degree of flocculation of the clays at the time the body was made is very important. The load is that required to break a bar in a transverse strength test.

(6) *Relationship between Sodium Silicate Compositions and Viscosity of Clay-Water Suspensions.*

Sodium silicate solutions are used quite commonly in the ceramic industries as deflocculating agents for clays, sodium carbonate being another

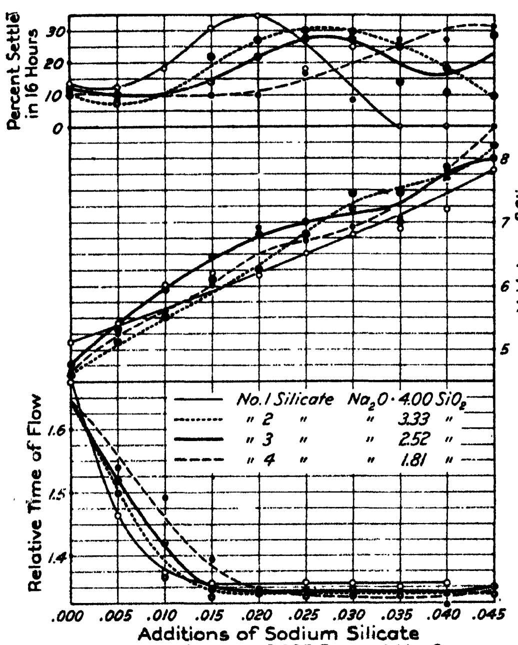
common substance used for the same purpose. As there are available sodium silicates with varying ratios of Na_2O to SiO_2, the experimental work of (a) McDowell and (b) Silk and Wood is of great interest. McDowell [25] used 4 varieties (Table 8), and determined their effect on viscosity, pH value and nthe rate of settling of clay-water suspensions of 2 ball clays and 4 China clays and kaolins.

TABLE 8.

Silicate	No. 1	No. 2	No. 3	No. 4
	Per Cent			
Na_2O	6.34	9.12	13.63	19.32
SiO_2	24.47	29.37	33.17	33.87
H_2O by Difference	69.19	61.51	53.20	46.81
Molecular Ratio $Na_2O:SiO_2$	1:4	1:3.33	1:2.52	1:1.81
pH Value	10.25	10.50	10.75	11.55

Figures 13 and 14 show some curves for an English China clay and a Tennessee ball clay, using a ratio of water to clay of 2:1 by weight.

The conclusion is reached that the sodium silicates low in soda and high in silica, namely those between compositions $1Na_2O.3.33SiO_2$ and $1Na_2O.4SiO_2$

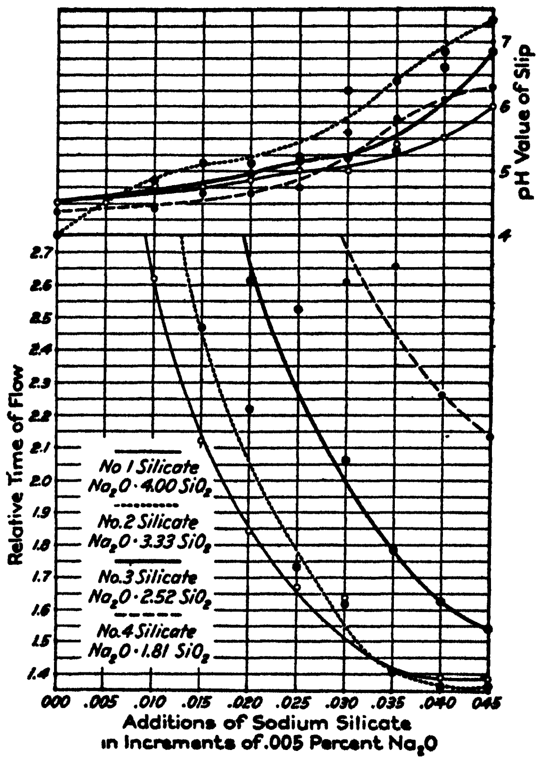


Courtesy J. Am. Ceramic Soc.

FIG. 13.—Effects of addition of sodium silicate to English china clay.

are the most effective deflocculating agents for a given Na_2O content. In some studies comparing the silicate solutions of $1Na_2O.4SiO_2$ with Na_2CO_3 and NaOH solutions, the sodium silicate solution was found to be a better deflocculating agent; i.e., on the basis of Na_2O additions, less corresponding sodium

silicate was required. In explaining this feature McDowell states that "The probable reason that sodium silicate is a more potent deflocculating agent is due to the presence of colloidal silica which adsorbs the Na^+ ions thus disturbing their equilibrium with the OH^- ions and allowing the latter to become more active in forming hydroxyl-ion complexes with the positive charged particles and ions on the clay particles and allowing the clay particles to reach maximum charge for that particular solution. It is, therefore, necessary to specify the agent used when giving the pH value at which a clay reaches minimum time of flow." However, he has found that silica sol alone is not a



Courtesy J. Am. Ceramic Soc.

FIG. 14.—Effect of addition of sodium silicate on Tennessee ball clay.

deflocculating agent. The silica solution contained 1.21 per cent SiO_2 and was made into a solution containing the same amount of SiO_2 as No. 1 sodium silicate solution. The pH value of the silica solution was 5.2.

There are no radical changes in the pH curves around the points corresponding to maximum fluidity (maximum deflocculation). The pH values for the maximum fluidity varied between 4.3 and 6.9, occurring on the acid side of the neutral point.

Silk and Wood[87] studied the same problem, using clay slips as well as an earthenware slip to determine the effect on their viscosities of the changes in soda-silica ratio of several silicates of soda, whose compositions (Table 9) were:

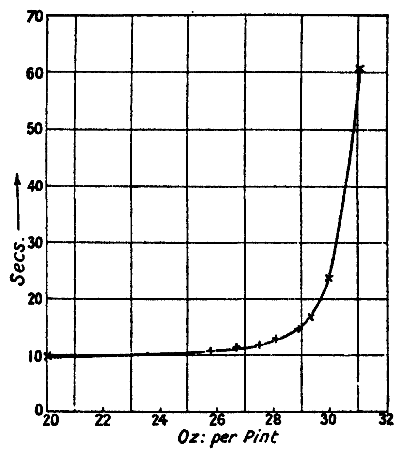
TABLE 9. *Composition of Some Silicate Solutions.*

Silicate No.	VW	U 65	P 84	L 100	H 112
	Per Cent				
Na_2O	6.45	7.16	9.50	11.65	13.80
SiO_2	24.88	26.26	30.50	32.85	32.90
H_2O by Difference	68.67	66.58	60.00	55.50	53.30
Molecular Ratio $Na_2O:SiO_2$.	1:3.95	1:3.80	1:3.3	1:2.9	1:2.5

A China clay slip alone, showed an increase in fluidity as the silica ratio of the electrolyte increased. These results are in accord with the findings of McDowell. The addition of 1.5 per cent whiting gave similar results, except that the fluidities as a whole were lower. The effect of the addition of whiting was determined because the earthenware slip later to be considered contained calcium carbonate.

The results obtained with the earthenware slip are, however, contrary to what was expected, and deserve mention. Figure 15 shows the relation between time of flow and slop weight in ounces per imperial pint (at 31 ozs. per pint 1 gram of slip contained 0.5777 grams of dry matter. A good casting consistency was obtained with 30.5 ozs. per pint). The slip contained 0.01 per cent Na_2O added as silicate P. 84. The curve shows how important it is that in comparative studies the water content be maintained constant.

Additions of the various sodium silicates were made and the fluidities measured. With no addition the time of flow was 34.2 seconds, which dropped to 13 to 15 seconds on the addition of 0.01 per cent Na_2O as silicate. The results of further additions are given in Figure 16—graphically. It is to be noted that varying the additions from 0.01 to 0.08 per cent Na_2O caused the fluidity to drop, but not very greatly, for each silicate used. Of greater importance is the fact that as the silica ratio of the electrolyte increased the general tendency was for the fluidity to remain constant (or to show a slight decrease). These results stand as an example of the difficulty of interpreting the mechanism involved in so complex a system. With regard to the effect of sodium silicates as electrolytes, these authors state that it seems reasonable to suppose that in dilute solutions, the silicates with a lower proportion of silica than $Na_2O.2SiO_2$ hydrolyze to produce NaOH and $Na_2O.2SiO_2$, where as the silicates with a higher silica ratio decompose to form $Na_2O.2SiO_2$ and colloidal silica.



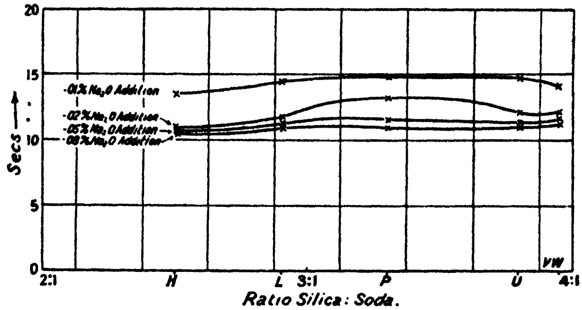
Courtesy Trans. Ceramic Soc., England.

FIG. 15.—Relation between time of flow and slop weight.

(7) *Electrical Conductivity of Clay-Water Suspensions.*

The electrical conductivity (or resistance) of a clay-water suspension changes with the ionic condition of the suspension, and such measurements have been made and reported on. Fessler and Kraner [85, 86] have made studies in the plant and laboratory in the attempt to correlate for a given porcelain body slip the pH, the electrical resistance and the viscosity. The resistance

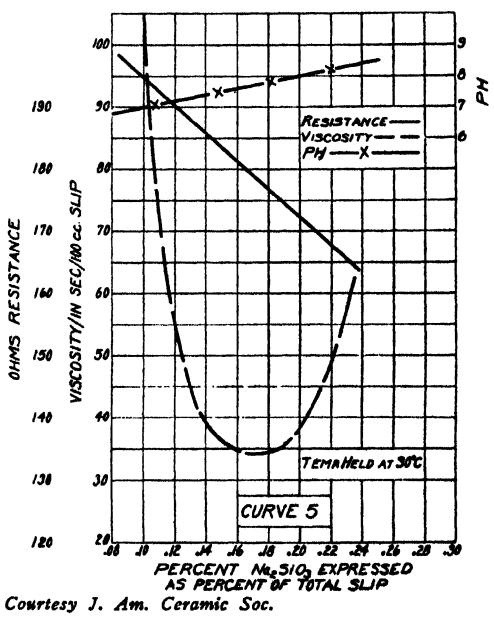
of the slip between two platinum electrodes was measured, applying 125 volts and alternating current. Figure 17 shows the effect of increasing the electrolyte, sodium silicates, in a body containing English China clay, English ball



Courtesy Trans. Ceramic Soc., England.

FIG. 16.—Relation between soda-silica ratios and time of flow.

clay, Kentucky ball clay, Georgia kaolin, flint and feldspar. The resistance measured in ohms continually decreases as the electrolyte additions are made, the pH values increase and the viscosity, measured by the flow time, reaches



Courtesy J. Am. Ceramic Soc.

FIG. 17.—Effect of sodium silicate on viscosity of a body mixture.

a minimum and then rises again. These investigators have also made measurements to determine the effects of other electrolytes and of stirring time, temperature and specific gravity on the resistance, pH value and viscosity. Their results given in the form of curves, are for brevity given here merely in a qualitative manner in Table 10.

Two kinds of slip are given, the casting slip used for casting porcelain, and the plastic body slip used for the plastic porcelain process. The plastic slip was taken from the factory system before going to the filter presses.

TABLE 10. *Relation between Electrical Conductivity and Viscosity of Porcelain Body Slips.*

Increase in	Kind of Slip	Resistance (ohms)	Viscosity (flow in seconds)	Changes Occurring in pH
Stirring time	Casting	Increases slightly	Decreases rapidly at beginning	No change
Stirring time	Plastic	No change	No change	No change
Temperature	Casting	Decreases rapidly	Decreases rapidly	Increases slightly
Temperature	Plastic	Decreases rapidly	Decreases slowly	Increases slightly
Specific gravity	Casting	Decreases slightly	———	No change
Specific gravity	Plastic	Decreases more rapidly	———	No change
NaCl content	Plastic	Decreases rapidly	Increases rapidly	No change
Na_2SiO_3 content	Casting	Decreases rapidly	Decreases rapidly to a minimum then increases	Increases rapidly
$AlCl_3$	Plastic	Decreases rapidly	Increases rapidly	Decreases rapidly
Mg SO_4	Plastic	Decreases rapidly	Increases rapidly	Decreases only fairly rapidly

(8) *Absorption of Ions by Clays in Water-Suspension.*

(a) *Hydrogen- and Hydroxyl-Ions.*—Several investigations have shown that an alkaline solution becomes less alkaline by the introduction of some clay into the solution, and that an acid solution becomes less acid after a clay has been added. These changes in pH have been followed by titration as well as by pH determinations.

Hall [11] has considered the question of how the ions are combined with the clay particles, whether by chemical action, physical adsorption or solid solution. Considering adsorption on the surface of the clay particles as being a major possibility, deviations from Freundlich's equation expressing this phenomenon were considered.

$$\frac{x}{m} = KC^{\frac{1}{n}}$$

x is the amount of (electrolyte) material in grams adsorbed by m grams of clay. C is the concentration of electrolyte in the solution at equilibrium, i.e., after the clay has adsorbed as much as it will, and K and $n (n > 1)$ are constants depending upon the substances used. The equation is such that plotting $\log \frac{x}{m}$ against $\log C$ gives a straight line relationship, $1/n$ being the rate of change between these two variables.

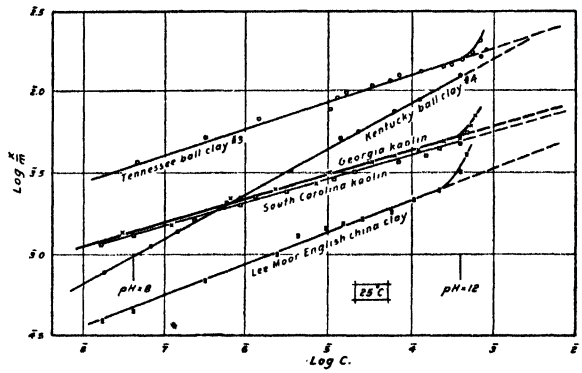
When C has the value of unity, K represents numerically the amount of solute adsorbed $\frac{(x)}{(m)}$. As the adsorption increases with the greater area of surface exposed, K is considered an index of the degree of subdivision of the particles.

Figure 18 represents the relationship between $\log \frac{x}{m}$ and $\log C$ for a number of clays and shows that the adsorption phenomenon represents quite completely the removal from solution of electrolytes between the pH values of 7 and 12, for straight line functions are obtained. Above pH 12 the straight

lines curve upward, showing relatively much greater removal of electrolyte from solution and indicating probably the introduction of chemical action between electrolyte and clay.

(b)—*Hydrogen and Chlorine Ions.* In some factory scale experiments the writer added 0.1 cc. concentrated HCl to 100 cc. of porcelain slip, which then showed a pH value of 4.3. After filtering by means of a filter press the filtrate showed a pH value of 5.0, showing that the clay-feldspar-quartz filter cake had adsorbed H-ions, causing the filtrate to become slightly more alkaline.

From another experiment made under semi-commercial conditions, the absorption of Cl-ions was determined. To 12 liters of slip (using 0.1 cc. conc.



Courtesy J. Am. Ceramic Soc.

FIG. 18.—Illustrating an approximate straight line relation between log. C and log. x/m over a range of concentration between pH 7 and 12.

HCl per 100 cc. slip) was added 5.15 grams Cl ion. After filter-pressing, the 4 liters of filtrate was found to contain by analysis 2.20 grams Cl ion, leaving some 4 grams Cl ion in the filter cake.

The experiments were conducted to determine the effect on the process of filter-pressing. By acidifying the slip the time required to remove the water from a filter press was reduced and the filter water was less turbid. Another effect was the absence of segregation in the filter cakes. These results were primarily due to the flocculation of the clays in the slip. In large blungers an addition of 0.5 to 0.75 cc. concentrated HCl per gallon of slip was considered sufficient. Insulators made of such acid-treated slip proved to be as good, mechanically and electrically, as insulators made of untreated slip.

(9.) *Plant Control Methods for Slips Used in Casting and Plastic Working.*

In some previous discussions examples have been given of methods used to determine the effect of electrolytes on the condition of a clay suspension or a body slip, such methods including viscosity, pH determinations, and electrical resistance.

It had been hoped by many that the development of methods and apparatus for making accurate pH determinations would yield reliable methods for slip control. So far these hopes have not been realized, and the only method involving electrolyte control which has persisted in good grace has been the viscosity method. Fessler and Kraner [85] stated "it would seem from the work so far that the H-ion concentration is not influenced as much as is the viscosity by the electrolytes present in the slips. The H-ion concentration values indi-

cate little variation whereas electrical conductivity indicates wide variation in slip condition which is not apparent throughout the plant processes." Randolph and Donnenwirth [22] conclude that the measurement of pH "cannot be substituted for other means of control, but may prove extremely useful and an important help in dealing with clays in slip and plastic forms."

Organic Matter as Protective Colloid for Clays.

The casting behavior [53] of a whiteware body mixture containing no ball clay (English China clay 50 per cent quartz 30 per cent, feldspar 20 per cent) was modified by the additions of organic matter in the form of tannic acid or peat muck. A casting slip containing as electrolytes 0.125 per cent of sodium silicate and 0.125 per cent sodium carbonate, cast in 30 minutes, and gave a transverse strength of 14.8 lbs. per sq. in. This mixture on standing overnight showed signs of local coagulation, making the slip appear lumpy. Adding tannic acid (calculated as 0.8 per cent C) to the slip changed its properties, for less water was needed to obtain a fluid casting slip; the casting time increased to 180 minutes, and the strength increased to 31.6 lbs. With peat muck (as 0.8 per cent C), less water was needed for casting, the setting time was 2 hours and transverse strength 27.9 lbs. In these respects the organic matter acted as a deflocculating agent. The addition of the organic matter also prevented the local coagulation on standing, and thus acted as a protective colloid.

As the organic matter (determined as per cent carbon content) increases in China clays, Scripture and Schramm [54] have shown that the plasticity and toughness increases. English China clays showed variations from 0.024 to 0.112 per cent C, North Carolina kaolin contained 0.084 per cent C, Florida kaolin 0.135 per cent and an English ball clay 1.40 per cent. These examples indicate the importance of organic matter as colloids in the non-plastic clays. More information is given under the heading of "Compounding of Porcelain Mixtures for Casting Process."

Molecular Changes in Clay Due to Heating.

The internal changes occurring on heating clay has been the subject for much experimentation and speculation. Most methods of attack have been tried, including thermal analysis, solubility of preheated samples in chemicals, and X-ray analysis. It is here possible to give only some of the typical results, which have been assembled in the form of a table (Table 11) showing the progress made in the past twenty years.

There are several points upon which there is general agreement: (1) Up to a temperature of about 500° C. heat is absorbed by the clay in a normal manner, because no internal changes are taking place. (2) In the range of 500° to 700° C. there is a decided reaction involving a large heat absorption. Water of crystallization is removed in this region from the kaolinite molecule $Al_2O_3.2SiO_2.2H_2O$. There is much evidence including direct loss in weight measurements for this statement. What happens to the remaining aluminum silicate at this period is still controversial. The earlier workers thought that the molecule was broken down to free alumina and silica, whereas the later workers are inclined to assume a rearrangement involving a complex aluminum silicate. (3) In the range of 800° to 950° C. at some fairly definite temperature there is a heat evolution involving a molecular rearrangement. (4) Above 1,000° C. there is a final rearrangement involving the formation with a heat evolution of an aluminum silicate in a microcrystalline form which becomes rather prominent at higher temperatures (probably 1,200° C. and above). These needle crystals were isolated and analyzed and it was assumed that their

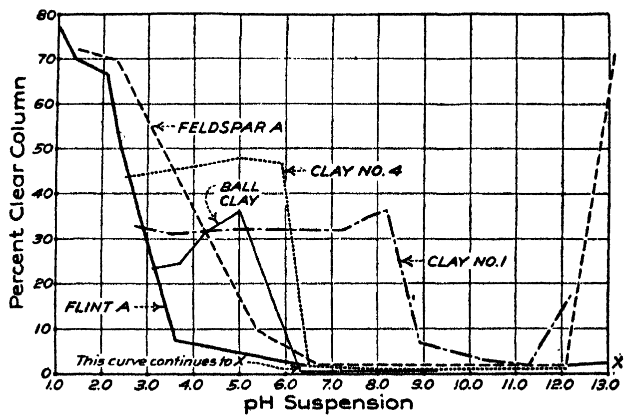
composition corresponded to the molecular formula $Al_2O_3.SiO_2$, and these crystals were named sillimanite, to correspond with a mineral found in nature whose general properties they resembled. Later work involving equilibrium studies showed that the composition $Al_2O_3.SiO_2$ was not stable at its melting point and that the stable compound had the formula $3Al_2O_3.2SiO_2$ known now as mullite.

The work of Hyslop and Rooksby [58, 59] involving X-ray studies shows their latest change based upon some work of Hansen and Brownmiller,[60] who experimented on the crystalline structure of precipitated alumina heated to successive temperatures. Hyslop and Rooksby were able to identify γAl_2O_3 and sillimanite ($Al_2O_3.SiO_2$) as being formed at 870° C. in clay. Around 1,060° C. both of these crystalline forms disappear and mullite crystals take their place and persist as the only crystalline form stable at these higher temperatures.

McVay and Thompson [61] have reported on X-ray studies made on a Georgia kaolin and on an English China clay. They found that heating the Georgia kaolin to 950° to 1,100° C. gave them an alumina pattern. This was not observed for the English China clay. Mullite was observed to form in both clays beginning at 950° C. Cristobalite was found in the Georgia kaolin when fired to temperatures of 1,225° C. and above, and was determined both by X-ray analysis and by thermal expansion measurements. Cristobalite was found in much smaller amounts in the English China clay fired to 1,250° to 1,275° C. The cristobalite comes, it is claimed, from the dissociation products of the kaolinite molecule.

The Behavior of Clays, Ground Feldspar and Quartz in the Presence of Electrolytes.

Scripture [26] made a series of solutions of water and electrolytes (using HCl and NaOH) and measured H-ion concentrations in terms of their pH values. To these solutions were added in one series 20 per cent by weight



Courtesy J. Am. Ceramic Soc.

FIG. 19.

of ground potash feldspar and in the second series 20 per cent by weight of ground quartz. The suspensions were shaken and then allowed to stand for 18 hours in tall test tubes. The clear supernatant liquids were then subjected to a pH determination.

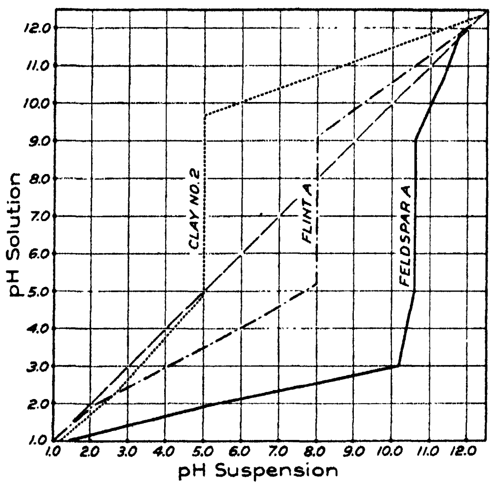
In Figure 19 is plotted the pH of the suspension against the height of

TABLE 11. *Internal Changes in Clays Caused by Heating.*

	Mellor and Holdcroft[55] 1910-11	Satoh[56] 1921	Vesterberg[57] 1925	Hyslop and Rooksby[58] 1927-28 (a)	Hyslop and Rooksby[58] 1927-28 (b)
(1) Heat absorption 0° to 500° C.....					
(2) Heat absorption reaction at	Beginning at 500° C.	650° to 700° C.		550° C.	500° C.
Breakdown of Molecule. Liberation of Water of Crystallization.					
Formation of ...	Free Al_2O_3 Free SiO_2	Free Al_2O_3 Free SiO_2	$Al_2O_3.2SiO_2$ a new form sol. in HCl	α cryst. phase ($Al_2O_3.2SiO_2$)	α cryst. phase + amorphous silica ($4Al_2O_3.3SiO_2+SiO_2$)
(3) Heat evolution reaction	800° C.	950° C.		870° C.	870° C.
Breakdown of ..	None	None		α cryst. phase	α cryst. phase
Formation of ...	Dense Al_2O_3	Polymerization of Al_2O_3		β cryst. phase + mullite ($3Al_2O_3.10SiO_2$ + $3Al_2O_3.2SiO_2$)	Sillimanite + γAl_2O_3 ($Al_2O_3.SiO_2$ + γAl_2O_3)
(4) Heat evolution reaction	1200° C.	1200–1300°		1060°	1060°
Breakdown of ..	None	None		β cryst. phase	Sillimanite + γAl_2O_3
Formation of ...	Sillimanite ($Al_2O_3.SiO_2$)	Sillimanite [$(Al_2O_3)_x + SiO_2 = Al_2O_3.SiO_2$]		Mullite ($3Al_2O_3.2SiO_2$)	Mullite ($3Al_2O_3.2SiO_2$)

the column of clear supernatant liquid. The taller the clear portion of the column the more flocculated or aggregated are the particles beneath the clear column. Both feldspar and quartz show similar types of curves as they are highly flocculated under strong acid conditions, and become deflocculated with the decrease in acidity. They maintain the deflocculated state over a wide range of further acidity decrease, and then show decided signs of flocculation as the suspension becomes quite alkaline. The quartz shows a wider range than the feldspar in which it will remain deflocculated. The clays show rather similar curves, except that the ranges of pH in which deflocculation exists are more narrow. The China clays show more limited ranges of deflocculation than the ball clays.

The changes in pH of the solutions due to the introduction of the finely divided feldspar and quartz are shown in Figure 20, where the pH values of the original solutions are plotted against the pH values of supernatant liquids of the suspension. Again the quartz and feldspar act very similarly. If the particles added were entirely neutral in their effect the supernatant liquid would have the same pH value as the original solution and the dotted curve (diagonal line) would represent the results.



Courtesy J. Am. Ceramic Soc.

FIG. 20.

In solutions of pH values between 1 and 3 the addition of ground feldspar causes the supernatant liquid to become much more alkaline. For solutions of pH 3 to 9 the supernatant liquid maintains a value of about 10 to 10.5 and above pH 12 of the solution the added feldspar shows little effect. Adding ground quartz to solutions of pH 2 to 5 causes the suspension to become more alkaline. For solutions of pH 5 to 9 the supernatant liquid maintains a value of about pH 8. With solutions of pH 9 to 12, the suspensions with quartz become slightly less alkaline. The quartz thus shows a reversal phenomenon, for below pH 8 of the solution, the quartz causes the suspension to become more alkaline than the solution, and above pH 8 of the solution the quartz causes the suspension to become less alkaline.

The addition of a China clay to solutions of pH 1 to 5 makes very little change in the pH, the slight change being towards the alkaline side. In solutions of pH 5 to 9.7 the clay maintains the suspension at a constant pH of 5.0. As the solution becomes more alkaline than pH 9.7, the clay additions cause rather rapid changes in the pH of the suspension towards the alkaline side.

Considering the diagonal "neutral" line as a line of reference the feldspar curve lies in the alkaline region, the clay curve lies in the acid region, and the quartz curve lies in both fields, crossing the "neutral" line. The three curves are, however, rather similar in shape and show definitely the ability of these materials to protect their suspensions from changes in pH, due to the addition of electrolytes. This is a kind of buffer action.

Particle Size and Particle Size Distribution of Clays, Ground Feldspar and Quartz

Feldspar and quartz are obtained in the massive form and are finely ground for use by milling in several ways, as in ball mills and in continuously fed tube mills. These minerals are sold to the ceramic trade according to fineness, the criterion being the amount of residue left on relatively coarse screens such as 100 and 200 mesh. These values give no information regarding the sizes and size distribution of the bulk of the particles. Clays and kaolins are naturally finely divided materials, needing only disintegration and the proper deflocculating conditions to disperse them. It is here understood that impurities such as quartz and mica have been removed from the clays by settling or other convenient means.

For comparison with the data to follow the particle sizes corresponding to standard mesh screens are given, the particle size in terms of the radius of a spherical particle (in millionths of a meter, μ) which will just pass through an opening in a sieve of a given number of spaces in a linear inch (Sieve Number or mesh per inch) (Table 12):

TABLE 12. *Particle Sizes Corresponding to Standard Mesh Screens.*

Radius μ	Standard Screen Sieve No.
73.5	100
52.0	150
37.0	200
30.5	250
22.0	325

Methods of Particle Size Determination by Sedimentation.

In Volume I of this series Odén [8] gives a number of sedimentation methods which may be applied to clays and other finely divided materials. Svedberg and Rinde have modified Odén's sedimentation balance and used a simple graphical method for interpolation of results. The percentage weight of sediment P falling from a column of the suspension is plotted against time. Drawing tangents to the curve at time t_1 and t_2 which by Stoke's Law correspond to radii of spherical particles r_1 and r_2, gives two intercepts p_1 and p_2 on the per cent weight axis. The numerical difference between p_1 and p_2 then gives directly the percentage of particles between radii r_1 and r_2 existing in the sample.

Schramm and Scripture [12, 13] have used a modification of Odén's method for determining points through which the curve can be drawn. They have studied commercial grades of pulverized quartz and feldspar, and clays. The writer has used the same modification for clays and has included his results in the same table for some individual clays which differ from the usual run. The modification consists in determining the amount of material settling out of a definite column of suspension held in a calibrated test-tube, after a definite period of time. This is obtained by siphoning off the suspension from the upper portion of the tube, determining the content of particles by weight and subtracting this weight from the weight of suspension calculated (or determined) in the lower portion of the tube. The quantity of sediment P expressed as weight per cent is plotted against the time of fall, and a curve obtained.

Table 13 gives the percentage distribution between certain arbitrary limits of radius of the particles. For the clays, particles greater than 14.3 μ radius

are grouped together, and for the feldspar and quartz, particles greater than 22.0 μ are grouped together, 22 μ radius corresponding to the finest commercial sieve used for control work. A glance at the data shows how coarse the ground minerals—feldspar and quartz—are in comparison with the clays and kaolins, this condition being especially noticeable in the amount of particles having a radius less than 1.7 μ.

The clays vary among themselves as classes, the English China clays and Florida kaolin having less fine material < 1.7 μ than the North Carolina and Zettlitz kaolins. The Tennessee ball clays are coarser than the English ball clays. It may be noted that the Zettlitz kaolin and English ball clays have rather similar distribution and particle size characteristics.

TABLE 13. *Distribution of Radius of Particles.*

Average of Radius μ	Quartz 2	Feldspar 5	English China Clay 10	Florida Kaolin 1	North Carolina Kaolin 1	Zettlitz Kaolin 1	Tennessee Ball Clay 2	English Ball Clay 4
	Per Cent							
>22.0	6.5	8.6	1.1	4.4	0.0	0.9	3.9	3.3
22.0–14.3	14.0	13.0						
14.3– 7.2	27.0	30.6	8.6	8.9	0.0	0.8	5.8	5.0
7.2– 3.2	22.1	20.2	20.5	19.2	9.6	8.6	10.5	6.5
3.2– 1.7	19.6	12.3	21.1	17.7	21.2	11.0	14.7	7.3
<1.7	10.8	15.2	48.6	49.8	69.2	78.7	65.0	77.8
	100.0	99.9	99.9	100.0	100.0	100.0	99.9	99.9

To show that particles of radius 1.7 μ and 14.3 μ are very different in size a table has been prepared showing the volumes and superficial areas of spherical particles having the radii considered in the table of particle size distribution, Table 14.

TABLE 14. *Volumes and Areas of Spherical Particles.*

$1\ \mu = 1 \times 10^{-6}$ m.
$1\ \mu = 1 \times 10^{-4}$ cm.

Radius	Diameter	Volume of Particles as a Sphere cc.	Surface Area of Particles as a Sphere sq. cm.
14.3 μ	28.6 μ	$12{,}250 \times 10^{-12}$	$2{,}570 \times 10^{-8}$
7.2	14.4	$1{,}564 \times 10^{-12}$	652×10^{-8}
3.2	6.4	137×10^{-12}	129×10^{-8}
1.7	3.4	21×10^{-12}	36×10^{-8}

Particle Size Determination of Silica Particles by X-Ray Diffraction Methods.

Aborn and Davidson [47] used the Scherrer method of determining the particle size of colloids by the broadening of the X-ray diffraction lines on a series of very carefully sized powdered quartz ranging in average size from 1.73 μ to 36.0 μ. As each particle gives rise to a diffracted spot on the photographic plate the total effect from a powdered specimen will be a general "peppering" of spots. As the particles become smaller the individual spots will become smaller, and as more particles will be in the path of the beam there will be greater tendency for overlapping and merging into continuous bands or rings.

They came to the conclusion that size distribution played so important a

TABLE 15. *Porcelain Batch Compositions.*

Porcelain Type	Sèvres [7]	Berlin [7]	Chinese [7]	Seger [7]	Bone China [7] A	Bone China [7] B	Bone China [7] C	Dental [7] A	Dental [7] B	Dental [7] C	Chemical [7]	Vitreous Hotel China [8]	Semi-Vitreous China [8]	Electrical Porcelain [30]	Porcelain Statuary Body [30]	Earthenware American [71]	Earthenware English [72]
	Per Cent																
Kaolin and china clay..	38	77	47	13.0	33–35	26	30	4	—	—	80	34	35	18	45	36	16
Ball clay	—	—	—	15.5	—	—	—	—	—	—	—	12	17	35	—	16	24
Feldspar	38	23	15	30.0	15–19	—	—	81	61	12	10	15	14	24	37.5	14	10
Flint or quartz........	24	—	38	41.5	10–14	—	—	15	29	60	10	36	35	21	—	34	50
Calcium carbonate	—	—	—	—	—	—	—	—	5	1	—	3	—	2	1	—	—
Bone ash	—	—	—	—	32–42	44	35	—	—	—	—	—	—	—	—	—	—
Cornish stone	—	—	—	—	—	30	35	—	—	—	—	—	—	—	—	—	—
Other substances	—	—	—	—	—	—	—	—	5	27*	—	—	—	—	—	—	—
Calcine	—	—	—	—	—	—	—	—	—	—	—	—	—	—	16.5†	—	—
Body matures at cone..	—	—	—	—	—	—	—	—	—	—	—	11	10	12	9	8	6

* Other substances; Borax 11, sodium carbonate 8, potassium carbonate 8, calcine feldspar (potash) 45, kaolin (Florida) 55%.

part that it was necessary to know this distribution before attempting to estimate the average particle size. Distinct qualitative differences were shown in the characteristics of the X-ray diffraction patterns for the following cases: (a) the same size distribution and varying average particle size, (b) varying size distribution and the same average particle size. Microphotometric analysis of the patterns yielded promising results for a quantitative relationship between pattern characteristics and average particle size when the size distribution was approximately constant. No satisfactory quantitative relation was found between pattern characteristics and varying size distribution.

Composition of Bodies.

Some typical batch compositions of porcelains, whiteware and earthenware are given in Table 15. The kind of ball clay and kaolin selected depends upon a number of factors: the plasticity desired for working the body, the firing range, the control of shrinkage, color. Highly fired bodies are usually low in ball clay content. The fineness of the batch will have a bearing upon the translucency and the micro-structure. The highly fired non-porous bodies are finely ground.

Riddle and Audley [73] have individually compiled a large number of body compositions, giving their batch mixtures as well as their ultimate chemical compositions. There are given also a number of physical, thermal and electrical properties for a large variety of electrical and laboratory porcelains, with some properties also for other ceramic ware.

Preparation of Bodies.

Compounding of the Mixture for Dry Process and Plastic Process Porcelain.

Blunging and Ball Milling.—The pulverized ingredients are weighed and mixed thoroughly with water. In some plants the ingredients are mixed in a blunger, a large vertical cylindrical tank agitated by paddles on a vertical shaft. In other plants the ingredients are put in ball mills with water and ground for a definite period of time.

There are numerous variations of these steps of the process. One variation is as follows: The ball clays are disintegrated dry and dumped into a blunger containing water, and made into a slip of density 1.15. The slip is then lawned on a vibrating screen to remove large particles of impurities as quartz and lignite. In the meantime the China clays, feldspar and flint are weighed into a ball mill, and the ball clay slip in the proper quantity is added. It is the usual practice to add raw porcelain scrap to the blungers or ball mills depending upon the process. The slip at this stage has a density of about 1.4 containing 40 per cent dry ingredients. Slip densities are usually given in ounces per pint or quart.

Filter Pressing.—For the mixing in a blunger and grinding in a ball mill excess water is used—and it is necessary to remove the excess before proceeding with the shaping of the articles. The common method is to pass the slip through a filter press. The water content of the filter press cakes is in the neighborhood of 20 to 25 per cent. The filter cakes are used mainly for the plastic process. For the dry process manufacture the filter cakes are dried still further and then disintegrated to give a product having 16 to 18 per cent water content. In several of the larger plants the slip is dried continuously in an apparatus having two drums (Filtration Engineers, Inc.). The first

drum revolves in the slip which is caused to stick to strings on the drum by the application of suction. The drying slip is slowly carried by the strings from the first drum to a second drum which is heated internally by steam. The semi-dried mixture on the strings is removed by metal fingers just before the strings dip into the slip tank. A moving belt carries the semi-dried material to a bin.

Wedging and Pug-Milling.—The filter cakes for the plastic process are then worked together to form a large plastic mass. In one method the filter cakes are put through a pug mill, and the extruding column removed in sections and beaten into a solid mass with mallets. After several days of storage, the plastic mass is cut into sections and put into another pug mill used for making shapes and blanks. In another procedure the filter cakes are put through two pug mills, the final column being immediately used for molding shapes.

Storage of the plastic mass in clay cellars is common practice. There are many variations in the conditions of storage, and many theories have been formulated to account for the changes in workability obtained. In general, it is agreed that there is a redistribution of the water, giving a more uniform moisture content, and that the plasticity of the mass is increased. Bacterial action has also been suggested to account for the increased plasticity.

Compounding of Porcelain Mixture for Casting Process.

Blunging and ball milling practice is essentially the same as for the other two processes. Electrolytes are added to the slip to put it in the condition of minimum viscosity. The electrolytes commonly used are solutions of sodium carbonate, sodium silicate and mixtures of these. Sodium bicarbonate is sometimes used. In all these additions, the essential factor is the hydroxyl ion.

The casting slip is maintained at a density usually between 1.75 and 1.80, and contains roughly 70 per cent dry ingredients and 30 per cent water.

One practice is to make a slip with a density of 1.4 and to pump the slip from one tank onto a lawn and into another tank where dry scrap is added to bring the density to the higher value.

The electrolytes are added as powders or as solutions and the quantities are checked by making viscosity determinations on the slips to obtain maximum fluidity. Viscosimeters in common use are of the efflux type, although in some plants the co-axial rotating cylinder type is used.

Casting Process.

It is the practice to keep the addition of electrolytes as low as po sible, for in the casting process the electrolytes pass into the plaster mold, and later as the plaster cast dries the electrolytes come to the surface of the plaster as salts. The salts are deposited in feathery crystals as an efflorescence on the plaster surface and interfere with subsequent castings. The deposition of the salts on the surface of the porcelain piece increases the alkali content and forms a glassy skin during the firing. On bushings such a skin is objectionable, and is the cause sometimes of breakdown. To avoid such breakdown, castings are often made thicker than required and the outer layer containing the excess salts is removed by trimming before firing.

Addition of Electrolytes.

(a) *Inorganic.*—In one factory 0.1 per cent Na_2CO_3 is used based on the dry weight of solids in the slip. In another plant mixtures of Na_2CO_3 and

sodium silicate are used to the extent of 0.2 per cent dry weight.[27] In a symposium on casting, values as high as 0.4 per cent of mixtures of "soda ash" and "water glass" were reported. Mention has already been made in the section on clay of the varieties of compositions of sodium silicate solutions obtainable and used in the industry. Unless the exact brand is known and the composition and concentration determined it is not possible to determine the exact quantities of alkali added. In the "casting" symposium [27] a recommendation was made for sodium silicate of composition Na_2O 13.7 per cent, SiO_2 32.9 per cent, H_2O 53.4 per cent, the $Na_2O:SiO_2$ ratio being 1:2.5. This ratio is lower than the 1:3.33 to 1.4 ratio limits suggested by McDowell [25] for the most effective deflocculating agents.

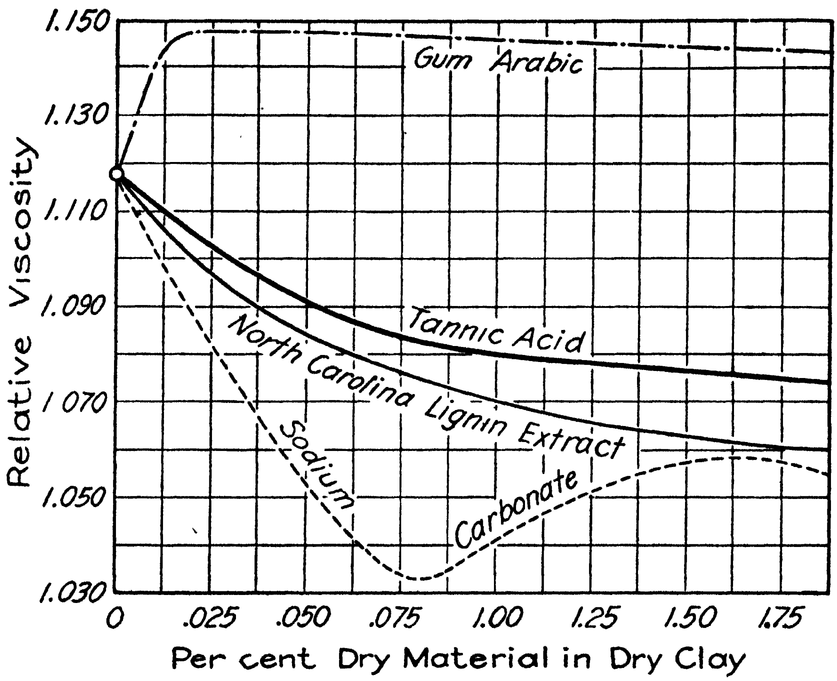


FIG. 21.—Effect of certain solutions on the viscosity of a 30 per cent clay dispersion.

A good account is given by Fritz and Donnenwirth [28] of their factory procedure in casting heavy electrical porcelains. Their casting slip is prepared by milling the ball clay, China clay and scrap porcelain in a ball mill with water and sodium silicate as electrolyte. After grinding 45 minutes the feldspar and flint are added and the whole mix ground 30 minutes. The density of the slip as it leaves the mill is 1.804 and a viscosity of 40 to 65 seconds flow for 100 cc. (orifice of viscosimeter 7/32 in.). The slip is put in an agitator overnight and in the morning the viscosity is found to be lowered to 35 to 55 seconds. It should be noted that the agitation lowers the viscosity.

(b) *Organic.*—Sanborn [29] suggests using first a mixture of sodium carbonate and sodium silicate, and secondly the addition of a Missouri clay containing lignite and which "seems to contain most of the electrolyte in the adsorbed state." The Missouri clay is substituted for part of the China clay. What appears to be a better explanation of the action of the organic material

is given by King,[46] who used a "lignin extract" and tannic acid to deflocculate clays and who suggests that these substances act as protective colloids (Fig. 21). While these organic materials are not as good deflocculating agents as sodium carbonate, they protect the clay slip by preventing or at least retarding the flocculation by other substances present. Gum arabic, which flocculates a clay slip, also acts as a protective colloid.

Shaping Processes.

There are three main processes of shaping porcelain mixtures and the condition of the mixtures is accordingly different for each process. In Tables 16 and 17 are given some data characterizing each process, as used in the manufacture of electrical porcelain maturing at cones 10-11.

TABLE 16.

	Dry Process	Plastic Process	Casting Process
Water content of working body	16–18%	22–24%	29–32%
Condition of body	Damp Powder	Plastic	Fluid
Shrinkages			
(1) From Mold to Fired State	14.5%	16%	16%
(2) From Dry (leather hard) to Fired State	12%	12%	12%

The shrinkages are based on the dimensions of the fired product. In large blanks made by the pug mill for the plastic process, the length of the column is allowed 2 to 4 per cent more shrinkage than the diameter.

Sometimes plastic and cast processes are referred to as the wet process, to distinguish them from the dry process.

TABLE 17.

	Dry Process	Plastic Process	Cast Process
Shaping	Pressing the damp powder in steel molds	Working plastic mass by applying hand or machine pressure as (1) Spinning-shaping on a potter's wheel by hand (2) Jiggering - shaping with a tool held in a machine (3) Extrusion by pug mill and other extruding machines (4) Pressing into metal and plaster molds by machine	Casting in plaster molds
Product of shaping	Finished shapes	Blanks and finished shapes	Blanks and finished shapes
Other operations.	Trimming cleaning	Dry blanks are (1) turned on a lathe and (2) shaped on a wheel using metal tools Finished shapes trimmed and cleaned	Dry blanks (1) turned on a lathe and (2) shaped on a wheel using metal tools Finished shapes trimmed and cleaned

Special Treatment of Body Slips and Plastic Masses.

Evacuation of Slip.—Lapp [31] has maintained that evacuating the slip (the water suspension of a porcelain body) before going to the filter press has beneficial effects. The advantages are that laminations are easily removed in the pugging process, heavier walls can be extruded safely, and ageing of the plastic mass is not necessary as plasticity is immediately realized. It is stated that free gas in plastic clay (meaning here the porcelain body mass) is a major evil, weakening the bond, lowering the density and causing occasional pits, blebs and fissures.

Kraner and Fessler [32] have repeated the experiments and come to negative results as regards the final quality of the electrical porcelain studied. By measurement they found the slip to contain 1 to 1.3 per cent air by volume, whereas a bone-dry piece of porcelain (that is before firing) contains 30 per cent voids. No difference in dielectric strength could be detected between porcelains made of untreated and evacuated casting slips. No appreciable difference could be noted in impact transverse strength of electrical porcelains made from plastic bodies, the slip of one having been evacuated before filter pressing and the slip of the other left untreated.

Application of Vacuum and Pressure to Plastic Body.—Under the heading of "Plasticity and Algae Growth in Clay Masses," some work of Spurrier has been quoted, in which plasticity is increased or induced by subjecting the plastic mass to a vacuum and collapsing the mass by breaking the vacuum suddenly. Spurrier insisted too that entrapped air and gases caused a lowering of the plasticity.

Composition of Glazes.

A glaze consists of a mixture of materials in a fine state of subdivision, which is applied in a relatively thin layer to a piece of ware. In the glost or glaze firing the mixture melts to a glass *in situ* and forms a thin glazed coating. The ingredients for a glaze, consisting usually of a number of chemical substances, are prepared by ball milling in water for a long period of time. The glaze slip may be applied by dipping and by spraying. In the dipping process the article is submerged in the glaze and on removal allowed to drain. The dipping suspension may have a density of about 1.30. In the spraying process the suspension under pressure is forced through a nozzle against the ware, the suspension having a density of about 1.45. As the clay content is usually low, the glazes are agitated to aid in maintaining the desired suspension.

The composition of a glaze depends upon the type of ware to be glazed and upon the use of the ware. For hard wear and rough usage a high-fired glaze will be necessary. For chemical purposes and for ignition work, a high-fired glaze is again necessary. Where the ware is to be completed in one firing, the glaze is applied to the dried "green" body and the combination fired to the proper maturing temperature. Where the ware is to be completed in two firings, there are two variations (1) firing the body alone to a high temperature, covering with a low temperature glaze and then firing in glost to a low temperature, (2) firing the body alone to a low temperature, covering with a high temperature glaze and firing to an appropriate high temperature to mature both body and glaze. These are known as the single- and double-firing processes.

Since Seger's time it has been customary to calculate glaze compositions on a molecular weight basis reducing all constituents to the oxide basis. The

monovalent and bivalent oxides are grouped together—their sum as molecular weight proportions taken as unity, and the entire formula worked out on this basis. RO members include the bases K_2O, Na_2O, CaO, BaO, MgO, ZnO and PbO total 1.000, R_2O_3 members include Al_2O_3 and the RO_2 includes the acid oxides, SiO_2, B_2O_3. Seger developed leadless glazes for porcelain and formulated rules regarding the range of compositions of glazes best suited for porcelains, and these rules are still followed today to a great extent. It is necessary that a glaze and the body to which it is applied shall have somewhat similar coefficients of expansion and contraction, otherwise material divergence will lead to defects like chipping and crazing, depending upon whether the glaze is under compression or tension. Seger had determined rules whereby changes in glaze formulas could be made to correct for such faults.

A few glaze formulas and their batch weight equivalents have been included to indicate their range, Table 18. For some glazes it is desirable to take the soluble (in water) ingredients and combine them with part of the insoluble (in water) ingredients and by heat cause them to combine to form an insoluble (in water) product. In glaze work this product is usually termed a frit. It is ground and mixed with the remainder of the ingredients to complete the glaze. There are several instances in which nature has supplied a complete or a nearly complete glaze composition. Near Albany and vicinity on the Hudson River banks is found an Albany slip clay which can be used as a (brown-colored) glaze for electrical porcelain. Usually some feldspar and coloring oxides are added to the Albany slip. An ultimate analysis of the Albany slip yields: SiO_2, 56; Al_2O_3, 15; FeO, 3; Fe_2O_3, 6; CaO, 6; MgO, 3; K_2O and Na_2O, 5; Cr_2O_3, 0.5; MnO_2, 0.2 per cent. Ignition loss about 5 per cent.

Ceramic decorations may be applied either to the biscuited ware, as an underglaze decoration, or to the glazed ware as an overglaze decoration. The underglaze decorations covered with the glaze are usually fired to a high temperature, whereas the overglaze decorations are fired to a low temperature around 800° to 900° C. The colors are obtained from oxides added to ceramic materials very finely ground together. Adherence to the ware is attained by means of organic substances and adhesives, the decorations being applied as transfers and by brush. This branch of organic colloid chemistry cannot be considered here.

TABLE 18. *Molecular Formulas of Glazes.*

	Earthenware. American Glaze [71] No. (1)	American Glaze [71] No. (7)	English Glaze [72]	Porcelain Electrical [80]	Vitreous Hotel China [80]
K_2O	0.173	0.175	0.070	0.20	0.20
Na_2O	0.032	0.138	0.233	—	0.10
CaO	0.456	0.344	0.400	0.40	0.30
PbO	0.217	0.219	0.290	—	0.20
ZnO	0.122	0.124	0.	0.30	0.20
BaO	—	—	—	0.05	—
MgO	—	—	—	0.05	—
	1.000	1.000	0.993	1.00	1.00
Al_2O_3	0.238	0.240	0.251	0.50	0.30
SiO_2	2.300	2.320	3.164	4.00	3.0
B_2O_3	0.271	0.276	0.402	0.10	0.3
Maturing at cone	4–6	4–6	6	12	4–5

TABLE 18. (*Continued.*)

Batch Formulas.

	Glaze (1)[11] Parts	Glaze (7)[11] Parts
Feldspar	34.0	20.7
China clay	3.6	5.9
Whiting	15.0	12.0
White lead	19.7	19.7
Zinc oxide	3.5	3.5
Flint	—	24.0
Frit A	34.0	—
Frit G	—	23.0
	109.8	108.8

	Frit A Parts	Frit G Parts
Flint	24.0	—
Feldspar	—	13.3
Borax	4.38	18.5
Boric oxide	9.07	—
China clay	2.33	—
Whiting	1.07	—
	40.85	31.8

FIRING PRACTICE.

In actual firing practice much attention is given to the rate of firing to take care of the changes occurring in the clays. The dehydration period is known as the "water-smoking" period, and usually applies to the heating of bone dry ware to about 600° C. As the clays contain organic matter it is desirable to remove such matter by means of an oxidizing fire, and is accomplished in the oxidation period from about 350° to 1,000° C. Poorly oxidized ware does not fire white (or light in color) and may have other serious defects. The rate of firing will depend upon the amount of ware being fired, the size of individual pieces, the kind of kiln and fuel used.

The ware is dried either at room temperature by long standing or at higher temperatures in shorter periods of time in driers (with or without humidity control). For firing, the ware is assembled in saggers (refractory clay containers) which are stacked in the kilns. The stationary type of kiln, either for up-draft or down-draft conditions is used for periodic firing, that is the ware and furnace are started cold, heated to the maturing temperature and cooled again. The continuous kiln or tunnel-car type of furnace requires a large production to maintain efficient and economic use. Saggers loaded with ware are stacked on the cars, which are slowly moved through the tunnel kiln. The high firing is done half-way down the length of the kiln, the hot air and gases from the firing zone heating up the incoming ware. In some cases muffle kilns are used for special ware and for heavy ware. The muffle is built gas-tight to prevent gases of combustion from coming in contact with the ware. It is, therefore, not necessary to inclose the ware in saggers, appropriate ceramic supports being used.

Reaching Maturity on Firing.

Each substance or material composing the body will go through its characteristic changes and reactions on heating until such temperatures are reached where interactions between substances will occur. The changes due to heat have been considered for individual materials like the clays, feldspars and silica minerals under the subject heads of these materials. Some discussion has also been given to the subject of the solubility of quartz and clay (separately and together) in feldspar at elevated temperatures. With the incipient formation of a vitreous mass due to the melting of the feldspar, the interaction between the feldspar and the other ingredients, and the vitrification of the ball

clays, the body begins to show a decided shrinkage. The shrinkage and the formation of a glass-like mass are the two visible features of the higher temperature firings. In ware like earthenware and wall tile, the amount of magma formed is not as great as in the porcelain types of ware and in general the shrinkage will not be as great. This phenomenon can be followed readily from temperature to temperature by measuring the shrinkage or the porosity. A graph (Fig. 22) is given to show the drop in pore volume (as per cent of the total volume) plotted against position in the tunnel kiln (as car numbers) for electrical porcelain. From Car 22 on, the porosity drops very

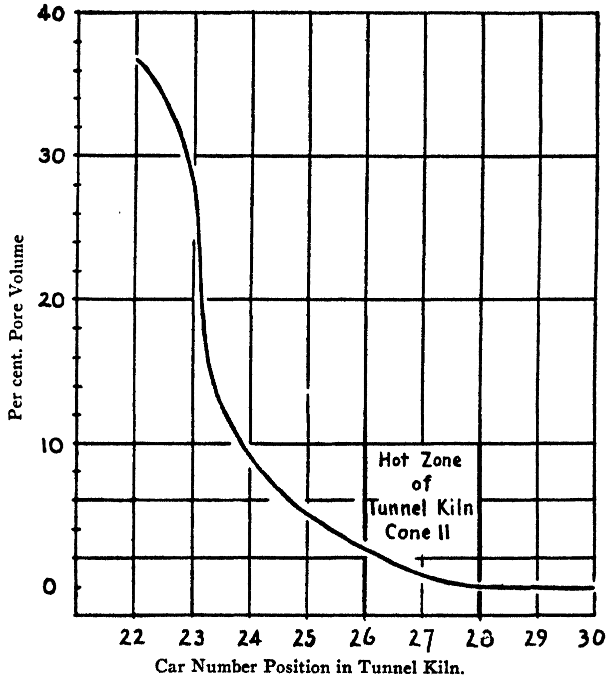


FIG. 22.—Change in pore volume on firing electrical porcelain in a tunnel kiln.

rapidly at first, then drops more slowly near the position of Car 25. Cars 26, 27 and 28 are in the hottest part of the tunnel kiln, and the porosity of their contents shows how they shrink and become non-porous when Car 28 is reached. The wetting of the substance by the magma and surface tension play a large part in effecting the production of a non-porous mass. Another curve (Fig. 23) is given for a European hard porcelain showing changes in both shrinkage and pore volume as a function of temperature, the data being taken from Rieke's [44] paper. Overfiring of the porcelain causes the formation of gases within the ware, and results in a swelled or bloated piece.

Effect of Varying Firing Time on Coefficient of Expansion.

A porcelain body containing clays, feldspar and quartz was fired at cone 12 for 16, 30 and 40 hours, the average coefficient of expansion being

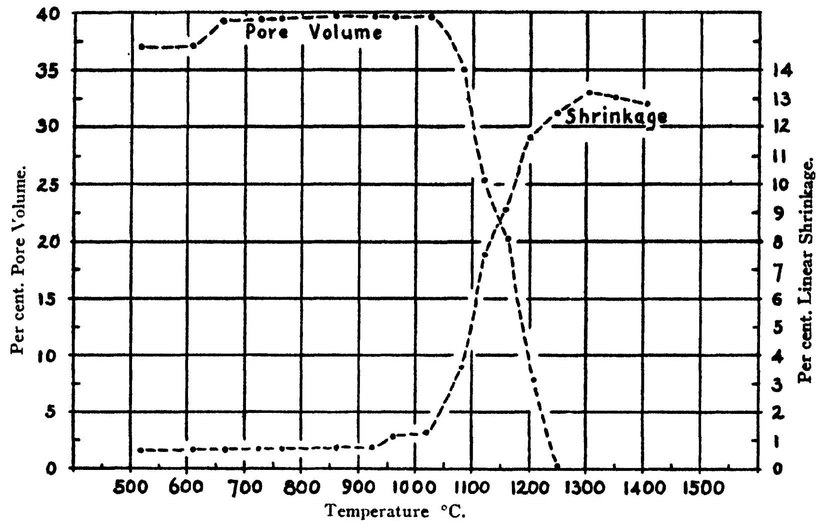


FIG. 23.—European hard porcelain. (After Rieke.)

measured.[76] From the data, it is shown that relatively large quantities of quartz remain undissolved after 16 hours' firing. This is shown by the large expansion between 560° and 580° C. corresponding to the α-β quartz inversion. After 30 hours' firing the free quartz content has been reduced considerably, and after 40 hours the free quartz content is eliminated almost entirely. (*See* Table 19.)

TABLE 19. *Effect of Firing Time on Coefficient of Linear Expansion.*

Firing Time in Hours	Average Coefficient of Expansion: Room Temperature to 680° C. $\times 10^{-6}$	Room Temperature to 560° C. $\times 10^{-6}$	560° to 580° C. $\times 10^{-6}$	580° to 680° C. $\times 10^{-6}$
16	7.0	7.3	16.0	4.0
30	6.0	6.5	7.0	3.2
40	5.3	5.4	5.0	4.6

Translucency of Porcelain.

Translucency of porcelain is greatly influenced by raw material make-up and by firing. Rieke and Samson[78] have determined that in general when the refractive indices of substances embedded in the porcelain matrix approach that of the matrix, the more translucent is the body. Mullite with a refractive index of 1.64 is less desirable than quartz, 1.55, as the refractive index of the matrix is 1.48. In general translucency is increased by raising the temperature of firing, increasing the feldspar content at the expense of the quartz, grinding the quartz finely, adding small quantities of fluxes, fritting or fusing quartz and feldspar before making the body. Translucency is decreased by repeated firings as the mullite crystals develop in size and quantity. Some clays and quartzes give better translucency than others. True solution of all the ingredients to form a glass will give greater translucency than a colloid suspension.

HEAT REQUIRED TO FIRE CERAMIC MATERIALS AND PORCELAIN BODIES.

A number of investigators have used the method of mixtures whereby the heated specimen is dropped into a calorimeter and the total heat given up to the calorimeter determined. The method is satisfactory provided it is realized that the results obtained tell only what has happened thermally to the specimen during the "cooling" interval. White [63] has measured very accurately the specific heats of quartz and other silicates in this manner. As the transformations in quartz are reversible, quartz has been used as a comparison standard in other methods of determining specific heat and the values accepted for both "heating" and "cooling" intervals.

The method of mixtures has been used for clays, and specific heat in the "cooling" intervals calculated as 0.2 to 0.3. These values were used for some years to represent the heat required to fire clays, that is, in the "heating" interval, and subsequent work has shown such use to be erroneous. Navias [64] first measured directly by means of a calorimeter the specific heats of clays in the "heating" interval and obtained an average value 0.51. The same method gave an average value of 0.24 for the "cooling" interval of the same clays. The results are given in Table 20 and illustrate the behavior of several clays, especially the large heat absorption of three clays in the "heating" interval, 420° to 900° C., and the heat evolution in the same clays in the "heating" interval, 900° to 1,200° C.

Cohn [65] and MacGee [66] have used differential thermal methods to obtain specific heats of a great many ceramic materials in the "heating" interval. From their curves they have also calculated the heat involved in a number of exothermic and endothermic reactions occurring in the heating of ceramic substances. Some of their data are given in Table 21, the data of MacGee having been calculated from his Table 7. It will be noted that where similar substances have been studied by these investigators, the values of Cohn are usually lower than the values of MacGee especially in the lower temperatures. These experimenters have discussed their differences in print, and the variation seems to be due to differences in method and technique. The higher values of MacGee for interval specific heats of clays agree with the values found by Navias by the direct calorimetric method.

MacGee gives data for Georgia kaolin, Delaware kaolin and Florida kaolin, their values being rather similar to those of the North Carolina kaolin. The Pennsylvania feldspar contained 10 per cent K_2O and 3.05 per cent Na_2O. The specific heat of chalcedony (and flint) is lower than that of quartz.

Cohn has experimented with a high-fire porcelain and its glaze. The porcelain was a Berlin porcelain containing clays 55.0 per cent, quartz 22.5 per cent and feldspar 22.5 per cent. The glaze was intended to mature at cone 16. In comparing the data for the "green" porcelain and the "fired" porcelain, it should be borne in mind that the first firing of a green porcelain removes the water of crystallization of the clays, and consequently the fired specimens weigh less. The data for the "green" porcelain are all calculated on the original weight of green specimen, whereas the data for the "fired" specimen are calculated on the weight of the dehydrated specimen.

MacGee has given some general conclusions which are of great interest, only those involved in the subject of this paper being quoted:

"(1) All *kaolins* undergo an endothermic process in the neighborhood of 575° C., which amounts to about 100 calories per gram of clay; (2) all *kaolins* undergo an exothermic process in the neighborhood of 960° C., which amounts to about 25 calories per gram of

clay; (3) it requires about 500 calories to heat one gram of any *kaolin* from 0° to 1,000° C., the specific heat over this interval being about 0.5; (4) *ball clays* undergo an endothermic reaction in the neighborhood of about 550° C., which amounts to about 90 calories per gram of clay; (5) *ball clays* undergo a slight exothermic reaction in the neighborhood of 975° C., which amounts to about 5 calories per gram of clay; (6) it requires about 450 calories to heat one gram of *ball clay* from 0° to 1,000° C., the specific heat over this interval being about 0.45."

TABLE 20. *Interval Average Specific Heats*[66] *(Navias).*

Temp. °C.	North Carolina Kaolin	A-1 English China Clay	Tennessee Ball Clay	Raw Flint Clay
"Heating" Intervals	Heat absorbed in calories per gram per degree			
25°- 420°	0.49	0.42	0.47	0.47
420°- 900°	0.69	0.95	0.53	0.68
900°-1200°	0.23	0.075	0.51	0.24
25°-1200°	0.50	0.55	0.51	0.50
"Cooling" Intervals	Heat evolved per degree of resulting weight of fired clay			
1200°-900°	0.23	0.17	0.20	0.19
900°-700°	0.28	0.31	0.33	0.32
1200°-700°	0.24	0.20	0.25	0.24

PETROGRAPHIC CHARACTER OF LABORATORY PORCELAINS AND WHITEWARE.

By means of the petrographic microscope, an examination can be made of the porcelain in either powder form or in thin section, and thereby determine the condition of the crystalline and glass phases, their distribution, their reactions and other properties. Audley [73] has given a fine succinct statement worthy of being repeated. He states as follows:

"The petrographic character of a ceramic body made from clay, feldspar and flint varies according to the proportions of the component materials and also with the method of preparation (involving physical conditions) and conditions of firing. In porcelains wide variations occur in the relative amounts of glassy matrix, undissolved quartz (or cristobalite) undecomposed or undissolved clay, and mullite . . .

"A good porcelain of the kind indicated should consist largely of a feldspathic glassy matrix with embedded crystals of quartz and mullite distributed evenly, but no visible particles of clay. The quartz should not exceed 20, or at most 25 per cent and the average size of its particles should not exceed 0.03 to 0.04 mm. diameter, all edges and corners being rounded off through partial solution in the matrix. The crystals of mullite should be numerous and well formed and should not exceed *ca* 0.01 mm. in length and 0.002 mm. in thickness. Porcelains answering to this description can be produced only at a comparatively high firing temperature. With lower temperatures small proportions of glassy matrix and mullite crystals are produced, the proportions diminishing gradually until the crystals cease to be formed and the amount of glassy matrix becomes relatively insignificant, and the product is no longer porcelain but simply white earthenware."

Many petrographic examinations of porcelain and whiteware have been made and recorded in the literature. A few photographs of thin sections are shown as illustrations. Insley [91] has made a study of six bodies of white earthenware, fired to different temperatures; namely, from cone 4 to cone 11. Two photomicrographs (Figs. 24 and 25) show the difference between a cone 4 firing and a cone 11 firing.

The cone 4 firing shows the quartz grains with sharp boundaries indicating no solution. The clay particles are amorphous grains without visible mullite

TABLE 21. *Interval Average Specific Heat.*

°C.	Zettlitz Kaolin (C)[65]	China Clay (C)[65]	A-1 English China Clay (M)[66]	North Carolina Kaolin (M)[66]	Kentucky Ball Clay (M)[66]	Norwegian Potash Feldspar (C)[65]	Pennsylvania Potash Feldspar (M)[66]	Rose Quartz (C)[65]	Rose Quartz (M)[66]	Chalcedony (C)[65]	Quartz (W)[67]	"Green" Porcelain (C)[65]	"Fired" Porcelain (C)[65]	"Green" Porcelain Glaze (C)[65]	"Fired" Porcelain Glaze (C)[65]
100	0.201	0.200	0.367	0.379	0.330	0.161	0.207	0.190	0.186	0.167	0.187	0.185	0.189	0.170	0.179
200	0.203	0.202	0.393	0.401	0.357	0.162	0.224	0.205	0.200	0.172	—	0.187	0.195	0.174	0.181
300	0.213	0.213	0.418	0.427	0.379	0.168	0.242	0.215	0.214	0.175	0.217	0.197	0.203	0.182	0.189
400	0.226	0.226	0.439	0.452	0.399	0.179	0.256	0.226	0.227	0.177	—	0.213	0.212	0.193	0.197
500	0.249	0.248	0.475	0.479	0.440	0.191	0.268	0.239	0.236	0.185	0.238	0.228	0.222	0.208	0.199
600	0.415	0.416	0.550	0.540	0.478	0.202	0.278	0.256	0.247	0.189	0.251	0.332	0.232	0.247	0.202
700	0.430	0.438	0.509	0.537	0.461	0.211	0.285	0.257	0.251	0.193	0.254	0.324	0.245	0.238	0.204
800	0.426	0.424	0.493	0.505	0.461	0.222	0.288	0.259	0.256	0.198	0.260	0.318	0.264	0.259	0.211
900	0.438	0.439	0.493	0.505	0.462	0.229	0.289	0.262	0.257	0.203	—	0.324	0.287	0.278	0.218
1,000	0.429	0.430	0.494	0.502	0.466	0.246	0.292	0.267	0.260	0.210	0.264	0.331	0.304	0.280	0.230
1,100	0.421	0.421	—	—	—	0.260	—	—	—	0.218	—	0.354	0.337	0.290	0.245
1,200	0.414	0.416	—	—	—	0.262	—	—	—	—	—	0.363	—	0.299	—
1,300	0.410	0.411	—	—	—	—	—	—	—	—	—	0.373	—	0.307	—
1,400	0.406	0.407	—	—	—	—	—	—	—	—	—	0.383	—	0.292	—

[65] (C) Cohn—between 20° and t°C.
[66] (M) MacGee—between 0° and t°C.
[67] (W) White—between 0° and t°C.

formation. There were remnants of the feldspar grains not completely melted. The cone 11 firing shows the quartz grains well rounded, and bounded by reaction rims. The clay particles are isotropic lakes containing well-developed mullite needle crystals. The ground-mass or magma is vitreous. The fairly low absorption is indicative of a well-bonded fairly non-porous body.

Courtesy J. Am. Ceramic Soc.

FIG. 24.

Courtesy J. Am. Ceramic Soc.

FIG. 25.

Klein [90] has made a fine study of some thirty commercial porcelain bodies and many other laboratory-prepared bodies. The photograph (Fig. 26) shows the development of mullite crystals and their extension into the glaze of a Royal Meissen chemical porcelain.

Courtesy U. S. Dept. of Commerce, Bureau of Standards.

FIG. 26.

As a general rule it may be stated that a material which will make a desirable addition product in a porcelain mixture should be either itself soluble or have contained in it a constituent which is soluble in the matrix of the porcelain. In other words it is necessary that the substance be "wetted" by the matrix in order to obtain a good bond between the constituents and thus form a strong porcelain. Such "wetting" can be detected under the microscope,

for a reaction rim will be found around the particle, which is losing its sharp outline by the solution.

Special Porcelains.

The main part of this paper has dealt with the porcelains and other ware made of the three classes of materials—feldspars, silica and clays. The special porcelains so designated here contain other substances, which replace in part or in toto the feldspar—which is the flux, and the silica—which is the inert constituent, of the porcelain. Substitutions for the clays are also made, both directly and indirectly.

Calcines and Calcined Materials.

For a number of types of porcelain ware it is a fairly common practice to calcine part of the batch, before introducing it into the main batch. A number of examples has already been given. Water-soluble constituents like boric acid, are mixed with insoluble constituents and heated to form an insoluble mixture or compound. Some calcines are synthetic fluxes, as for instance, those made by Bleininger and Riddle [82] for use in spark plug porcelains. The mixture $MgCO_3$ 23.85 per cent, kaolins 76.15 per cent calcined to cone 12 corresponds to $1MgO.1Al_2O_3.2SiO_2$—and the mixture $MgCO_3$ 18.20 per cent, kaolins 56.00 per cent, quartz 25.80 per cent calcined to cone 13, corresponds to $1MgO.1Al_2O_3.4SiO_2$.

The term "calcine" connotes some chemical reaction involving fusion, whereas the term "calcined" merely infers a heat treatment. Quartz and cyanite may be calcined to cause internal changes to take place, whereby permanent volume changes are effected, in these cases—expansions. Precipitated or low fired substances may be strongly heated to cause preliminary shrinkage. Clays may be calcined to remove volume changes and convert them to mullite and matrix. Shrinkage and warpage of bodies containing calcined materials are usually lower and under better control.

Compositions of Special Porcelains.

(1) Substitutions of Fluxes.

Beryl.—Beryl is a mineral having the composition $3BeO.Al_2O_3.6SiO_2$ equivalent to SiO_2 67 per cent, Al_2O_3 19 per cent, BeO 14 per cent. It has been used in porcelains, replacing some or all of the quartz, and replacing some or all of the feldspar. Twells [39] has summarized the results of a number of workers. Electrical porcelain bodies maturing at cones 10 to 11 could be made from clay 50 per cent, feldspar 13 to 24 per cent, flint 0 to 6 per cent, beryl 22 to 38 per cent. Beryl porcelains are noted for their ability to withstand heat shock, their low thermal expansion and high electrical resistance at temperatures above room temperature. Bleininger and Riddle [82] have made spark plug porcelains using kaolin 40 per cent, quartz 5 to 25 per cent, ball clay 10 per cent and beryl 25 to 45 per cent, the bodies maturing at cone 11 to 12. The bodies require careful temperature control in firing, and give high electrical resistance at high temperatures. The thermal expansion of these beryl porcelains was found to be lower than the feldspathic porcelains.

The writer has found rather marked differences in fluxing behavior between different lots of beryl, and the tendency to bloat in certain cases has been attributed to the presence of alkalies in the beryl. The higher the alkali content in the beryl the lower the maturing temperature of the beryl porcelain.

This tendency to bloat was experienced with the beryls themselves when fired as cones and examined under the microscope. Rows of very fine bubbles were found in those fired to the higher temperatures. The partial chemical analyses of beryls used in this work illustrate the point: (1) BeO 9.30, Na_2O 5.95, K_2O 0.56 per cent; (2) BeO 11.86, Na_2O 2.46, K_2O 0.54 per cent; (3) BeO 12.3, Na_2O and K_2O 5.5 per cent. Another remedy for the prevention of bloating in such instances has been the reduction in the quantity of feldspar added.

Calcined Bone.—The English potters have developed a bone-china body used chiefly for dinner ware. It is characterized by its whiteness and translucency. A typical formula is given by Heath [86] as calcined bone 45 per cent, China clay 25 per cent, Cornwall stone 30 per cent. The bone consists of ground animal bone, calcined to cone 4, and is considered to be represented by $Ca_3(PO_4)_2$. The bone ash is known to be a good flux. In place of Cornwall stone, potash feldspar and flint may be used. The body matures around cone 7 to 9. Davis [87] has used the mineral apatite from Canada as a substitute for bone ash. Its formula may be written $3Ca_3(PO_4)_2.CaF_2$, the calcium phosphate content being 92.25 per cent. A translucent body maturing at cone 9 had the composition apatite 32 per cent, feldspar 19 per cent, China clay 35 per cent, flint 14 per cent.

Lepidolite.—Lepidolite may briefly be described as a lithia mica, Dana giving as its molecular formula $3Li_2O.2K_2O.3Al_2O_3.12SiO_2.8F$. He believes that the ordinary Lepidolite is a mixture of the pure lithia mica and the pure potash mica, muscovite, $K_2O.3Al_2O_3.6SiO_2.2H_2O$. Twells [88] reports some experiments in which lepidolite was used as a flux, alone—and with feldspar in a porcelain body. The lepidolite contained SiO_2 50.18 per cent, Al_2O_3 22.81 per cent, CaO + MgO 0.34 per cent, K_2O 17.48 per cent, F 1.20 per cent, other constituents 2.51 per cent. The total alkali content amounts to almost 24 per cent. Lin [88] reports that the lepidolite powder shaped into cones had a deformation range of 1,080° to 1,110° C., whereas a potash feldspar had a deformation range of 1,260° to 1,290° C. Mixtures of feldspar and lepidolite had intermediate values for the deformation. Replacing feldspar with lepidolite in a porcelain mixture gave bodies which attained a non-porous condition at a lower temperature. The resistance to heat shock was quite great for the porcelains containing lepidolite.

Talc.—Talc or steatite is a mineral having the empirical formula $3MgO.4SiO_2.H_2O$ with a chemical composition MgO 31.9, SiO_2 63.3 and H_2O 4.8 per cent. The melting point is quite high, mainly about 1,540° C., and this melting point is lowered somewhat by impurities. Some actual melting points of different talcs are 1,450°, 1,515°, 1,530°, 1,545° C. Articles may be made from talc, either by machining them from the soft massive rock, or by pressing the talc powder, and firing the products. The rock need only be fired to about 1,000° (or above) to obtain rock-like pieces, whereas the compressed powder must be fired much higher. The addition of clay to talc, causes low-melting eutectics to form, which are easily understood from a consideration of the ternary system $MgO = SiO_2 = Al_2O_3$. A mixture of clay and talc in equal proportions has a melting point near 1,350° C. Thus talc is a good flux in the presence of clay and has been used to replace feldspar, clay and quartz in porcelain mixtures. It is characteristic of bodies containing fairly large proportions of talc that the maturing range is quite narrow, and great care is needed in reaching the correct firing temperature for a slight raising of the temperature causes a melting of the ware.

Talc has been used in heat-resisting bodies, as heater plates and spark plugs,

with success. Wataya [85] has analyzed European talc spark plug porcelains and has made similar bodies with equivalent properties. The porcelain best suited for the purpose contained 80 parts talc and 0 to 15 parts clay, a kaolin being preferred to a plastic clay. Lime as a fluxing agent gave poor results.

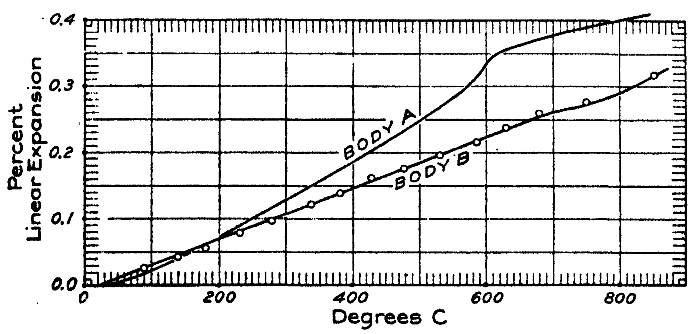
A talc body is recorded by Watts, King and Fisk [77] as containing California talc 47.5 per cent, ball clay (Tennessee or Kentucky) 25.0 per cent, Albian kaolin 10.0 per cent, Florida kaolin 10 per cent, potash feldspar 7.0 per cent, whiting 0.5 per cent. Both mixtures mature around cone 9½, the body made with the Tennessee ball clay being superior with regard to resistance to impact and resistance to heat shock, but inferior with regard to electrical resistivity at high temperatures.

(2) Substitutions of Inert Substances.

(a) **Oxides.**

Alumina.—Calcined alumina has been used by Bleininger and Riddle [82] in a spark plug porcelain body; kaolin 45.0 per cent, feldspar 17.6 per cent, calcined alumina 33.0 per cent, calcine 4.4 per cent ($MgCO_3$ 23.85 parts, kaolin 76.15 parts), maturing at cone 16. The electrical resistance at elevated temperatures was fairly good. The calcined alumina may be included in a calcine as for instance kaolin 70.2 parts, calcined alumina 27.8 parts, boric acid 2.0 parts, fired to cone 20.

Twells and Lin [88] worked on bodies replacing quartz with calcined alumina, the remainder of the batch being clays 48.5 per cent, feldspar 34.0 per cent.



Courtesy J. Am. Ceramic Soc.

Fig. 27.—Thermal expansion curves. Body A, typical electrical porcelain fired to cone 11. Body B, fused silica porcelain or "fusilain" fired to cone 8 under reducing conditions.

The bodies were fired to cones 8 to 12. With high alumina content, the shrinkage was lower, the resistance to heat shock lower, mechanical strength greater, and dielectric strength lower than with high quartz content in the electrical porcelain.

Fused Silica.—Fused silica obtained by melting quartz has been substituted for quartz in porcelain mixtures. Westman [16] compared two mixtures, one containing 20 per cent quartz, the other 20 per cent fused silica, the substitutions being made by weight. He found a marked difference between the two bodies in the way they matured, that is in the way they reached the stage of becoming non-porous. The quartz-containing body required a temperature of cone 10 to 11 under oxidizing conditions, whereas the fused silica-containing

body required a temperature of only cone 8 provided the furnace atmosphere was reducing. The thermal expansions of these two porcelains were different, the quartz-containing body showing the characteristic sudden volume change at the α to β inversion (575° C.), whereas the fused silica-containing body did not show this change (Fig. 27).

Zirconia.—Zirconia (ZrO_2) has been substituted for quartz in an electrical porcelain body of composition clays 48.5 per cent, feldspar 34.0 per cent, quartz 17.5 per cent by Twells and Lin.[88] Their mixtures were fired from cones 8 to 12. The zirconia gave the mixtures great ability to withstand heat shock, gave them greater mechanical strength and did not improve the dielectric strength (the voltage breakdown). The color was poor. Geller and Woods [89] made a series of porcelain bodies holding constant China clay 25 per cent, ball clay 10 per cent, kaolin 10 per cent, and varying the remaining 55 per cent, between feldspar 6 to 28 per cent and zirconia 27 to 49 per cent. With the high feldspar content the bodies matured around cones 6 to 8 and as the feldspar decreased, the maturing temperature reached cone 16. These bodies had good working qualities, good firing qualities and excellent mechanical strength. The electrical resistance at high temperatures was not very good. By removing the feldspar and substituting a calcine the electrical resistance was materially increased. The composition was ZrO_2 35 per cent, ball clay 5 per cent, kaolin 35 per cent, calcine 25 per cent ($MgCO_3$ 18.2 parts, kaolin 56 parts, quartz 25.8 parts, fired to cone 13), and matures at cone 14.

(b) Zirconium Silicate.

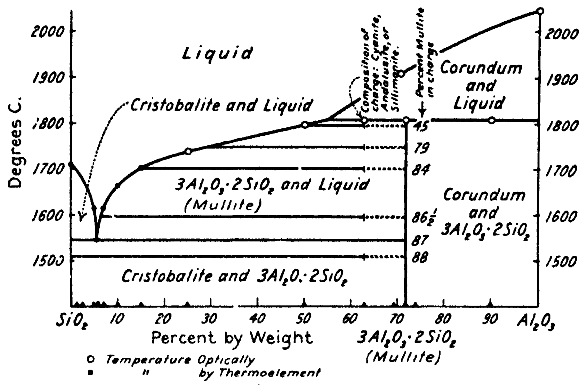
Watkin [45] has reported on the effect of substituting zirconium silicate (presumably the mineral zircon $ZrO_2 . SiO_2$) for flint in an electrical porcelain body. Greater tensile strength was obtained by a 10 per cent substitution, although the electrical properties were not materially altered. Bleininger and Riddle [82] made porcelains for spark-plugs using zircon 36 per cent, kaolin 37 per cent, ball clay 5 per cent, feldspar 18 to 22 per cent, calcine (kaolin 60.5 parts, $MgCO_3$ 39.5 parts) 0 to 4 per cent. The bodies matured at cone 13 giving mechanically strong porcelains, whose electrical resistivity at high temperatures was only fair. The use of beryl in place of feldspar as a flux may better the electrical properties. Geller and Woods [89] substituted zircon for quartz in a series of bodies, holding constant English China clay 25 per cent, ball clay 10 per cent, kaolin 10 per cent, and varying the zircon between 27 and 49 per cent, the remainder of the batch being feldspar 6 to 28 per cent. The maturing range was between cone 10 and cone 16, the high zircon bodies requiring the higher temperature. With the increasing zircon content, there was a marked tendency towards warping. The heat shock properties were good, and the electrical resistivity at high temperatures only fair.

(c) Aluminum Silicates (Non-Plastic). Minerals and Synthetic Products.

In the past decade much work has been done on the non-plastic aluminum silicates, as addition products for special porcelains. Formerly clays and kaolins were used in the calcined state as a source of non-plastic aluminum silicates, the calcined clay giving mullite and a siliceous magma. Now, minerals and synthetic products are used to a certain extent as the source of the non-plastic aluminum silicates. It is true of all aluminum silicates, as far as is known, that heating if carried high enough will disintegrate them, and convert

them into mullite and a matrix whose composition will depend upon the relative proportions of the oxides present. The amount of inversion to mullite depends upon the temperature and upon the influence of impurities, but there is a total theoretical amount of mullite formed which can be determined from the equilibrium diagram of the system $Al_2O_3-SiO_2$ (revised by Bowen and Greig [79] and given in Fig. 28) for any temperature.

The diagram also shows the composition of the minerals *andalusite, cyanite* and *sillimanite* and the amount of mullite obtained by conversion, the maximum quantity on cooling being 88 per cent. Table 22 gives a list of some of the minerals which have been used for the purpose indicated. The integers refer to the molecular proportions and the percentages to chemical compositions. Kaolin and mullite are given for comparison only. Except for dumortierite the other minerals have an excess of silica when converted to mullite by heat. Greig [79] has determined the manner in which mullite is formed from andalusite, cyanite and sillimanite, and Peck [80] has made a similar study. Cyanite has such a large volume change on firing that it is necessary to prefire it before adding it to the



Courtesy *J. Am. Ceramic Soc.*

FIG. 28.—Diagram showing percentage by weight of mullite formed by heating sillimanite, andalusite, or cyanite.

mixture. Cyanite shows decided mullite formation at 1,350° C., andalusite at 1,500° C. and sillimanite at 1,750° C. The state of the residual silica in each case is still a question.

Andalusite has been used in porcelain mixtures of several types. In cone 10 bodies andalusite has been substituted for quartz, the other constituents being clays and feldspar. For higher-fired bodies of the spark plug type, andalusite with clay and small quantities of flux have been used.

Porcelain bodies containing *calcined cyanite* have been prepared by McDowell and Vachuska.[83] They maintained a clay content of 50 per cent, using 10 per cent Kentucky ball clay, 10 per cent Tennessee ball clay, 10 per cent Florida kaolin and 20 per cent English China clay; and varying the feldspar, quartz and cyanite contents. The cyanite was calcined at cone 18 for two hours. Those bodies containing 30 per cent calcined cyanite, and over, showed properties not found in the ordinary porcelains. In these bodies, the modulus of rupture increased, the coefficient of expansion decreased, the firing range was increased, the maturing temperatures being cone 16 and above. A microscopic examination showed the calcined cyanite to act as an inert ingredient, there being no secondary formation of mullite. There are several manufac-

tured products made by treating cyanite and other minerals with fluxes and heat. Curtis [84] mentions one type, called Vitrox, which is of a fibrous nature. Tough porcelains have been made by its use, when substituted for part of the quartz content.

Bowen and Wyckoff [81] have studied the thermal dissociation of *dumortierite* and find that heating at 1,500° C. removes the water of crystallization and the boric oxide. Mullite is formed from the remaining alumina and silica with a slight excess of silica. Mullite is found from X-ray studies to appear at 1,200° C.

Pyrophyllite is a soft fibrous mineral—resembling talc in this respect and in its soapy feel. In the powdered form it is used as a substitute for talc in non-ceramic purposes. Additions of pyrophyllite have been made to porcelain mixtures to replace quartz as an "inert" ingredient. In dry process porcelain the quartz acts as an abrasive on the metal molds. Pyrophyllite is a soft mineral and has certain advantages on this account. At the temperatures of the porcelain kiln, cone 10, the mullite development is very slight.

TABLE 22. *Aluminum Silicates—Minerals.*

Mineral	Al_2O_3	SiO_2	H_2O	B_2O_3	F_2
Andalusite, Cyanite, Sillimanite	1	1	—	—	—
	62.9%	37.1%	—	—	—
Pyrophyllite	1	4	1	—	—
	28.3%	66.7%	5.0%	—	—
Dumortierite	8	6	1	1	—
	64.6%	28.5%	1.4%	5.5%	—
Topaz	55.4%	32.6%	—	—	20.7% (= 8.7) (0 = 2F)
Mullite	3	2	—	—	—
	71.8%	28.2%	—	—	—
Kaolin	1	2	2	—	—
	39.5%	46.6%	13.9%	—	—

TABLE 23. *Pyrometric Cone Equivalents.*[83]

Cone No.	Rate of Heating: 20° C. per Hour End Point* ° C.	150° C. per Hour End Point* ° C.	Cone No.	20° C. per Hour End Point ° C.	150° C. per Hour End Point ° C.
1	1125	1160	11	1285	1325
2	1135	1165	12	1310	1335
3	1145	1170	13	1350	1350
4	1165	1190	14	1390	1400
5	1180	1205	15	1410	1435
6	1190	1230	16	1450	1465
7	1210	1250	17	1465	1475
8	1225	1260	18	1485	1490
9	1250	1285	19	1515	1520
10	1260	1305	20	1520	1530

* The end point is the temperature at which the tip of the cone on deforming touches the support on a level with the base of the cone.

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Ceramic Refractories as Disperse Systems

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Introduction.—Ceramic refractories are manufactured from earthy materials some or all of the constituents of which are in a fine state of division previous to the firing operation. The colloidal aspects of the behavior of the raw materials during the processes which they undergo preparatory to firing, are similar in character to those encountered in the same operations with clay products and will not be discussed in this article, which will be confined to the behavior of the materials at high temperatures as influenced by the small size of the individual particles and the consequent large surface which they expose.

The following properties of, and phenomena associated with, the behavior of refractories at high temperatures may be appreciably influenced by the degree of dispersion of the material: Volatility, melting point, sintering, rate of transformation from one crystal form to another, rate of fluxing and of chemical reaction, amount and rate of shrinkage, porosity and pore size, and in extreme cases practically all physical properties, including true specific gravity and refractive index.

This behavior arises from the fact that the properties of small particles, either the drops of a liquid or the crystals of a solid, vary with the size of the particle when the particles are very small and also from the enormous surface exposed by a material in the dispersed condition as compared with the same material in the macro-crystalline form. The subject can perhaps best be further elucidated by discussing a few examples.

Volatility.—Certain refractories, for example magnesite bricks used for lining an electric furnace, have a rather high volatility at high temperatures and gradually distill away, at the same time depositing a layer of the material on the colder parts of the furnace and upon materials which are being heated in the furnace. This behavior in the case of magnesia, for example, is sometimes interpreted by the statement that magnesia has a comparatively high vapor pressure as compared, for example, with alumina or with crystalline aluminum silicate. In this connection, however, it should be remembered that vapor pressure, while important, is only one of the factors which determine the volatility of a material. The fact that the magnesia lining of a furnace may have a higher volatility and therefore a shorter life than alumina or aluminum silicate under the same conditions does not *necessarily* mean that magnesia has a higher vapor pressure than the other materials. It might indeed have a lower vapor pressure and yet exhibit a higher volatility.

The second factor which determines volatility is the amount of surface exposed, that is, the area, not of the face of the brick, but the contact area, magnesia-air. The greater the porosity of the refractory and the smaller the individual particles thereof, the greater will be its volatility, other things

being equal. The high volatility arising from a large surface exposure may indeed be so great as to make it impossible to melt a material even when it is placed in surroundings many hundred degrees above its melting point. This may be illustrated by the following experiments performed by the writer:

"In an investigation which had for its purpose the development of a simple and convenient apparatus for measuring the melting points of refractory materials, the arrangement illlustrated in Figure 1 was tried. A stick of magnesia was first prepared from the powdered material by compressing it in a suitable mold. After drying, the stick was placed in the holder and fed into the hottest part of the oxyacetylene flame as shown in the figure. Although the flame temperature is approximately 3,000° C. and the melting point of MgO is 2,800° C. it was found impossible to melt the end of the stick. Instead the stick gradually decreased in length owing to the volatilization of the magnesia.

"Refractory materials are known to have extraordinarily high latent heats of fusion[1] and consequently also very high latent heats of sublimation. Owing to the large surface

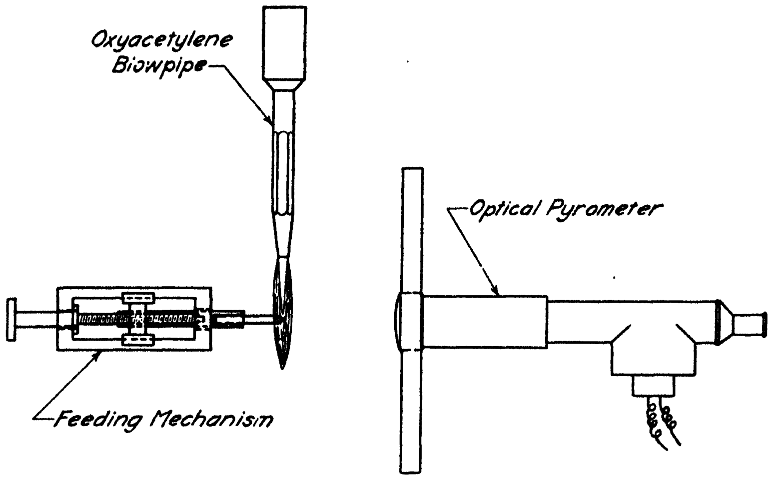

Fig. 1.—Apparatus for the approximate determination of the melting points of refractory materials. [Washburn and Libman, *J. Am. Ceram. Soc.*, **3**, 637 (1920).]

exposed by the particles of MgO which made up the stick in the above experiment, volatilization was sufficiently rapid to make it impossible to raise the temperature of the end of the stick to the melting point. That this explanation is the correct one was shown by the following experiment. A stick of dense coarsely crystalline magnesia was prepared with the aid of an electric arc. This stick was then fed into the oxyacetylene flame as before and the magnesia melted into drops on the end of the stick. In this experiment the surface exposed by the magnesia is comparatively small but volatilization is nevertheless greatly promoted by the strong draft of hot gas which sweeps across the end of the stick. In spite of these strong evaporating conditions it was, nevertheless, possible to bring the end of the stick up to and above the melting point, thus showing that magnesia in the non-dispersed condition does not have any very great vapor pressure even at its melting point."

Sintering and Shrinkage.—It is a well-known fact that a body made up of a large number of very small particles will, on heating, shrink in volume and usually also decrease in porosity. This phenomenon is known as "sintering." In general, sintering is promoted by both heat and pressure but will occur at temperatures far below the melting point of the material. Thus the sintering of mountain snows produces glacier ice.

Two properties of colloidal particles are important in connection with the mechanism of the sintering process. These are their higher vapor pressure and their lower melting point as compared with the same properties for the macro-crystalline material. If the temperature of the body is below the melting point of the material in the macro-crystalline form but above the melting point of the colloidal particles, the colloidal particles may melt, coalesce and then recrystallize in the form of larger crystals with a consequent shrinkage in volume. While this colloidal melting is a possible cause of sintering, it is probably not the one ordinarily encountered in firing refractory bodies since the temperatures ordinarily attained are not sufficient even to melt the colloidal particles. What takes place is probably the following: The body contains particles of varying sizes and the smaller the particle the higher its

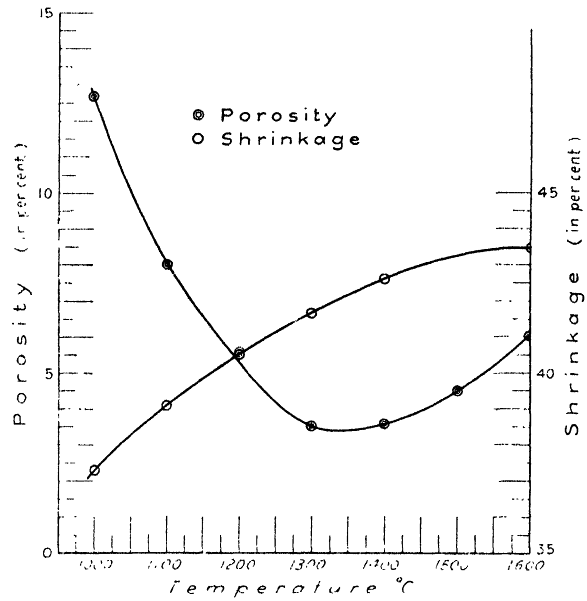

FIG. 2.—Sintering curves for zinc oxide. [Libman, *J. Am. Ceram. Soc.*, 5, 489 (1922).]

vapor pressure. Hence at temperatures where vaporization becomes appreciable the small particles can no longer exist in equilibrium with the larger ones. The small ones consequently disappear by vaporization and since their saturated vapor is at too high a pressure to be in equilibrium with the larger particles the vapor condenses on the larger particles, which thus continue to grow in size at the expense of the smaller ones, until finally the resulting mass consists of a coarse aggregate of comparatively large closely interlaced crystals.

If the refractory body contains two materials which are capable of entering into a chemical reaction with the production of a compound (e.g. SiO_2 reacting with Al_2O_3 to produce aluminum silicate) then, regardless of the relative sizes of the various particles, the dissociation pressures of the compound will always be less than the vapor pressures of the substances from which the compound is formed. Whenever, therefore, a temperature is

attained at which the compound can form at an appreciable rate by reaction of the vapors, the reacting substances will gradually disappear and the body will thereupon be transformed into an aggregate of coarse crystals of the compound.

Figure 2 shows some curves illustrating the sintering of zinc oxide at high temperatures. The test pieces were small cylinders prepared from pure precipitated ZnO by the dust-press process. The furnace was heated at the

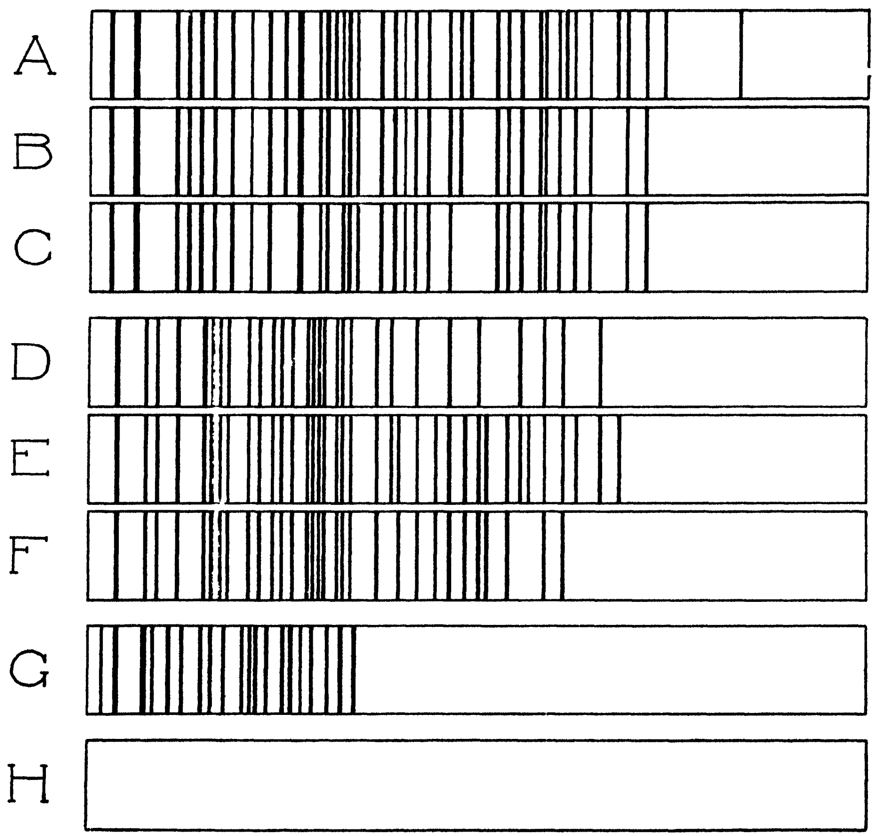

FIG. 3.—X-ray crystal spectra.
A, quartz crystal; B, raw flint; C, raw chalcedony; D, cristobalite; E, calcined flint; F, calcined chalcedony; G, tridymite; H, silica glass.

rate of 200° C. per hour and trials were drawn every 100° C. beginning with 1,000° C. The volume-shrinkage curve shows that the body shrinks uniformly with increase in heat treatment but its porosity passes through a minimum when 1,350° C. is reached. This peculiar behavior is doubtless due to the gradual growth of large crystals at the higher temperatures and a consequent development of small cracks or interstices between them. The completely sintered body showed the development of crystals, some as large as 0.5 mm. in diameter.

The Firing Behavior of Chalcedony.—Chalcedony is usually described as a cryptocrystalline form of silica. The individual crystals are microscopic or sub-microscopic in size but their X-ray diffraction pattern (*see* Figure 3) shows that they are crystals of quartz. In other words, chalcedony may be described as a closely compacted mass composed of highly dispersed quartz together with small amounts of water and other impurities. On heating, the water is driven out and the remaining material will analyze as high as 99.87 per cent SiO_2. It is thus a very pure quartz, differing from ordinary massive quartz chiefly by the high degree of dispersion, that is, by the extreme smallness of the individual crystals. Chalcedonic rocks, in which class is included flint, constitute one of the raw materials employed in the manufacture of refractory bodies and by comparing the properties and behavior of chalcedony (colloidal quartz) with the properties and behavior of ordinary massive quartz the influence of the colloidal constitution of chalcedony may be illustrated.

When quartz is calcined at high temperatures it is transformed into the crystalline form of silica known as cristobalite, this transformation being accompanied by a marked decrease in specific gravity. The transformation of colloidal crystals is however ***much more rapid*** than that of massive or macro-crystalline quartz and the resulting cristobalite is moreover also made up of colloidal crystals and hence differs from ordinary or macro-crystalline crystobalite in certain of its properties. The influence of this high degree of dispersion upon the physical properties of cristobalite is evident from a comparison of the properties of calcined chalcedony (colloidal cristobalite) with those of ordinary cristobalite as illustrated in Table I. The specific

TABLE I.—*Comparison of the Properties of Calcined Chalcedony with those of Cristobalite.*

	Calcined Chalcedony		Cristobalite	
	α	β	α	β
Specific gravity, 25°/25°	2.175	...	2.33	...
Index of refraction	1.456—1.470	...	1.484	...
Inversion temperature, t_1	...	220°	...	244°
Coefficient of cubical expansion near t_1				
(*a*) Cc. per gram per deg. $\times 10^6$	1.3± 0.3	1.4± 0.2	1.1± 0.5	1.5± 0.4
(*b*) Per cent per degree $\times 10^3$	2.7± 0.6	2.8± 0.4	2.4± 1.1	3.2± 0.8
Volume increase on inversion $\alpha \longrightarrow \beta$ at t_1				
(*a*) Per cent	2.63		2.83	
(*b*) Cc. per gram $\times 10^4$	131		132	

gravity and the index of refraction show an especially marked difference. That the calcined chalcedony is actually made up chiefly of cristobalite crystals is however demonstrated by its behavior on inversion as shown in the table

and also by the fact that its X-ray diffraction pattern is identical with that of cristobalite. The X-ray diffraction patterns of various forms of silica are shown in Figure 3.

REFERENCES.

[1] Cf. Washburn, *Trans. Am. Ceram. Soc.*, **19**, 199 (1917).
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The Colloidal Nature and Properties of Cements and Mortars

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Although the use of many cements and mortars dates back to prehistoric times, their nature is by no means clearly understood and many of the investigations which have been made in order to ascertain what occurs when a cement or mortar sets or hardens have done little more than show the extreme complexity of the changes involved. There is, therefore, abundant scope for further investigation of most of the problems involved in the production and use of cements and mortars, and the purpose of the present paper is to summarize the conclusions which have been drawn from the very numerous observations which have been made, in order to form a starting point for further investigation and research. The available data is, at present, insufficient for any simple explanation to be found which is applicable to all cements and mortars.

Varieties of Cements and Mortars

Cements and mortars may be divided into two chief groups (*a*) Inorganic, and (*b*) Organic.

Inorganic Cements

Inorganic cements and mortars may be subdivided into seven groups, namely:

Siliceous cements including Portland cement, natural cement, rock cement, Roman cement, grappier cement, and the various cements which are analogous to Portland cement, such as slag cement, iron Portland cement, etc.

All these cements are made by heating a mixture of calcium carbonate, silica and clay (or the equivalent of these substances) to such a temperature that partial fusion or sintering occurs. Such mixtures may occur naturally, the essential ingredients being present in suitable proportions (as in the "natural" cements) or they may be made artificially from any suitable materials which may be available. Thus, *Portland cement,* which is the most accurately compounded of the siliceous cements is composed of a carefully adjusted mixture of calcium carbonate—usually in the form of limestone or chalk—and a siliceous clay. It may be made equally well from an argillaceous limestone (which is a natural mixture of clay and calcium carbonate) by the addition of either limestone or siliceous clay, so as to make the composition of the final mixture suitable for the production of Portland cement. Very similar cements may be made by heating a mixture of limestone and slag or other waste siliceous products, provided the composition of the mixture is properly adjusted and no deleterious substances are present.

Numerous patents have also been granted for the production of Portland and similar cements from various waste materials of a calcareous nature. One

of the most recent * consists in blowing powdered ashes containing unburnt fuel through a jet with compressed air and lighting the mixture as it is projected from the jet. This method is of interest in countries where lignite and other low-grade fuels rich in ash occur in abundance, but in other areas its commercial value is more doubtful. The sulfates present in most calcareous ashes would prevent them being used for cement, unless such sulfates could previously be removed in a cheap manner. The use of calcium carbonate recovered as a by-product in various chemical industries and of alkali-waste as raw materials for the production of Portland cement is mentioned in many text-books, but its commercial application is small.

In order to secure the requisite accurate adjustment, elaborate precautions are taken by the manufacturers to ensure the "raw mix" being composed of extremely small particles which are mixed together in the most thorough manner possible, the composition of the mixture being ascertained by analysis and any necessary adjustments made before it is sent to the kilns. By this means, a Portland cement is produced which is remarkably constant in chemical composition and physical properties.

Ordinary Portland cement is composed of:

	Range (Per Cent)	Normal (Per Cent)
Lime	61–67	63
Silica	20–28	26
Alumina	4–9	8
Iron oxide	0.5–6	3

It is customary to express the composition in terms of what is known as Michaelis' *Hydraulic Modulus* which is found by dividing the percentage of lime by the sum of the percentages of the other three constituents.

$$\text{Hydraulic modulus} = \frac{\text{lime } \%}{\text{silica } \% + \text{alumina } \% + \text{iron oxide } \%}$$

It is generally understood that the hydraulic modulus should not be less than 1.7 and it may, with advantage, be between 1.7 and 2.3.

In addition to the constituents above mentioned are various others, but they are mainly *impurities* and in such small proportions that they need not be described here.

Sulfates are not necessarily impurities, as gypsum ($CaSO_4.2H_2O$) is added to the clinker prior to grinding to regulate the rate at which the cement sets (see *Retarders, infra.*).

The addition of slag to a Portland cement usually increases the proportion of sulfur trioxide (SO_3) to beyond the 2.75 per cent allowable in most specifications.†

Free lime is present only in a badly made Portland cement.

During the last fifteen years or more, there have been many attempts to improve the quality of Portland cements. These improvements consist chiefly in (*a*) the use of purer limestone or chalk and clays or equivalent "earths"; (*b*) the more accurate proportioning of the various ingredients; (*c*) the finer grinding of the raw materials; (*d*) the more complete mixing; (*e*) the better control of the kiln; (*f*) the finer grinding of the clinker, and (*g*) the skilful

* Eng. Pat. 168,406.

† The American Standard Specification allows 2.00 per cent of sulfur trioxide to be present. The following limits must not be exceeded: MgO, 5 per cent; loss on ignition, 4 per cent; insoluble residue, 0.85 per cent.

use of gypsum or other materials to regulate the time required for a pasty mixture of cement and water to set hard. In some modern cements, a larger proportion of lime and a smaller proportion of alumina are used than in the cements made twenty years or more ago.

Whilst ordinary Portland cement has been greatly improved in quality, the chief improvement is observable in what are known as super-cements or Rapid Hardening Portland Cements, described later.

Super-cements and *rapid-hardening Portland cements* are made in the same manner as ordinary Portland cements, but they contain rather more lime, are burned at a higher temperature and are much more finely ground. In other words, they are made more skilfully and with greater accuracy. Haegermann [1] has shown, however, that whilst extremely fine grinding increases the rate of hardening, it does not, alone, convert ordinary cement into super-cement. Filostofow [2] has shown that extremely finely ground, neat Portland cement has a lower tensile and crushing strength than coarser cement and that the coarser particles are equally as active as the finer ones, but require a longer time. He obtained the best results with a cement which passed 70 per cent through a sieve with 10,000 holes per sq. cm. (250 per linear inch). A 1 : 3 mixture of cement and sand (unlike neat cement) increased in strength in direct proportion to the increase in fineness.

It is customary to use limestone rather than chalk and a more siliceous clay (with a silica: alumina ratio of 3 : 1) than is commonly used for ordinary Portland cement.

They have a hydraulic modulus between 2.0 and 3.0 and a standard 1 : 3 mortar made with one of these cements is as strong at 2 and 7 days as those with ordinary Portland cement at 7 and 28 days respectively. Care must be taken not to confuse rapid-hardening cements with those which set quickly; the best rapid-hardening cements set rather slowly, but become hard soon afterwards.

In a rapid-hardening Portland cement, the residue on a 180-mesh sieve should not exceed 0.5 per cent, that on a 200-mesh 1.5 per cent and 98.5 per cent should pass through the 200-mesh and of this 80 per cent should be separable by a current of air flowing with a velocity of 21 ft. per min. corresponding to 0.01 mm. size. It is only the "flour" which gives the early strength, and the real value in this respect should be deduced from the proportion of flour and not of "residue."

Table 1 shows the average composition of ordinary Portland cement, rapid-hardening Portland cement and aluminous cement (*ciment fondu*):

TABLE 1. *Average Composition of Cements.*

	Lime	Silica	Alumina	Iron Oxide	Hydraulic Modulus $\frac{\text{Lime}}{\text{Other Constituents}}$
Ordinary Portland Cement.......	60–64	18–21	4–7	1–4	1.7–2.0
Rapid-hardening Portland Cement	62–70	18–24	4–8	2–3	2.0–3.0
Ciment fondu	35–45	5–12	35–45	5–12	0.5

It has been shown by Kühl that cements with definitely high or definitely low silica are superior in strength to those with intermediate proportions. This is recognized in practice, the two kinds having a modulus of 3.4 to 4.0 and about 1.4 respectively.

The high silica cements are made by adding sand, quartz or flint to a Port-

land cement mixture and raising the burning temperature. The cements with a low silica content or a high proportion of alumina are made by adding bauxite, with iron ore as a flux, or by definitely using a mixture suitable for an aluminous cement (*see* later).

The addition of large proportions of feldspar to the ordinary constituents of a cement mix is worth investigation.

Aluminous cements (*cf. infra.*) are also "rapid-hardening," but are of a wholly different type; they are regarded as too costly for general use, so that when the term "rapid-hardening cement" is used it generally refers to a Portland cement possessing this property.

The distinguishing feature of all rapid-hardening cements is that although they set no faster than ordinary cement, and thus allow as much time for necessary manipulation, the rate at which they harden has had very favorable consequences in the practice both of work poured on the site and of precast objects. In each case, the effect is to lessen the time for which work done has to wait before it can be used, so not only reducing the time occupied in construction from weeks to days, but enabling the shuttering to be removed proportionately more rapidly and used again, with a notable saving in the quantity required on the job, and generally in the amount of idle time for which all material is held up. The advantage in some kinds of work is, indeed, more than is expressed merely by the saving to the contractor. The substitution of rapid- for slow-hardening cement in road work, for instance, enables the work to be completed and the road reopened to traffic in a fraction of the time that would be required otherwise, and its use for piles permits a similar acceleration of the process of driving them. A further advantage of using rapid-hardening cement is found in cold weather in the fact that the period during which concrete is injured by frost ends when the material has reached a certain stage of hardness and it has been found that where protection against frost is required with ordinary cement concrete for two days after it has been placed, it is unnecessary with rapid-hardening cement after 24 hours. The difference is still more marked with the more costly aluminous cements. The heat generated during hardening is, moreover, considerably greater with rapid-hardening than with ordinary cement, or at least it is generated in a much shorter time and thus increases the temperature of the mass proportionately, so serving as an automatic protection against frost, which in some instances may be sufficient to make other kinds of protection unnecessary.

At the same time, experience has confirmed the remarkably greater strength obtained by the use of these rapid-hardening cements, and the absence of any countervailing disadvantage, allows advantage to be taken of the actual strength of the material in the calculation of designs. Important authorities are tending to increase the permissible load on concrete structures where approved rapid-hardening cements are used.

Rapid-hardening Portland cements of good quality comply with all the Standard requirements for a first quality Portland cement.

Iron Portland cements are made by mixing basic slag with a suitable proportion of limestone, the mixture being ground and heated in a kiln in the same manner as when making ordinary cement. Such cements usually contain more iron oxide than ordinary Portland cements; they also contain about 3 per cent of manganic oxide almost wholly in the celite. In such cements, the celite is a mixture of a compound of the type $2CaO.R_2O_3$ with a calcium aluminate and dicalcium ferrite. In one case investigated by Guttmann and Gille [8] the celite was $4CaO.Al_2O_3.6Mn_2O_3.O \cdot 4Fe_2O_3 + CaO.Al_2O_3$. Under

normal conditions all the manganese is present as manganic oxide, but if the alumina content is low, tetravalent manganese may also be present.

The slag used in the manufacture of these cements varies greatly in composition and with it varies that of the finished cement. A fair average composition of Iron Portland cement is:

	Per Cent
Lime	54–62
Silica	20–25
Alumina	4–11
Iron Oxide	2–8

The *hydraulic modulus* should not be less than 1.7.

The term "Iron Portland Cement" is sometimes applied to two other materials:

(*a*) A cement made from iron ore (hematite) of low iron content (which is used instead of the clay or equivalent in ordinary Portland cement) and limestone. This cement differs from ordinary Portland cement and from iron Portland cement. Its most important use was in the Panama Canal.

(*b*) A simple mixture of quicklime and slag, which is commonly known as a *slag cement.*

True iron Portland cement can be used for most of the purposes for which ordinary cement is used. Its chief importance is not due to its properties, but to the facility it affords to certain firms to convert waste slag into a commercially saleable product.

Slag cements are mere mixtures of slag and slaked or hydrated lime and partake more of the nature of mortar than a cement. They must, on no account, be confused with a cement made by heating a mixture of slag and lime to incipient fusion, as in the manufacture of iron Portland cement.

Small differences in the composition of the slags greatly affect the cement produced from them. Slags rich in alumina produce good cements when ground with calcium sulfate and a "developer of hydraulicity," such as lime or Portland cement clinker, the best results being obtained with a mixture of 86 parts of slag, 8 of lime and 3 to 9 of calcium sulfate.

The slags used for such cements may be regarded as metastable glasses which are attacked by water and in the presence of lime produce similar hydraulic products to those from the hydration of Portland cement. Yet though the products are similar, they do not appear to be identical, and slag cements are much weaker than Portland or iron Portland cements.

The strength attained is almost wholly due to the fineness of the slag-particles. Feret has shown that a very little lime will actuate the slag and produce a cement. Slag cements are regarded as being very resistant to sea-water.

Blast furnace cement is another form of slag cement which is made by granulating basic slag by rapid cooling and mixing it with 15 to 69 per cent of Portland cement. The composition should be such that

$$\frac{CaO + MgO + \frac{1}{3}Al_2O_3}{SiO_2 + \frac{2}{3}Al_2O_3} > 1.0$$

The basic slag need not be made in a "blast-furnace," this term being a common mistranslation of the German "High Temperature Furnace" and usually indicating an open hearth furnace.

Some slag cements and iron Portland cements are made with as much care as Portland cements and are correspondingly constant in their properties,

but the so-called "Natural Cements," "Roman Cements" and other siliceous cements, in which less care is taken to adjust their composition, are much more variable and uncertain in use. On the other hand, the natural and Roman cements can, sometimes, be manufactured much more cheaply than Portland, slag and iron Portland cements, and in places where a larger quantity of an inferior cement will serve the same purpose as a superior, yet more costly, cement, the "natural" cements may be preferred on account of the difference in cost.

Natural or *rock cements* were known long before Portland cement, being made in a similar, but more crude manner from argillaceous limestone containing clay and calcium carbonate in suitable proportions. Hence, the value of these cements, like that of the rock from which they are made, depends on the nearness with which their composition approaches that of Portland cement. It is usually necessary to sort the most highly cementitious pieces from the material drawn from the kiln, the remainder being inferior in quality or even useless. Owing to the lack of adjustment in composition, it is by no means unusual for one-quarter of the burned material to be rejected. Natural cements are usually much coarser than Portland cements, but during the last few years, finer grinding has been customary to make cements which are better able to compete with Portland cement.

The great drawback to natural and rock cements is their unreliability. At the present time they are not much used outside Europe; their chief purpose appears to be to form a cheap rival to Portland cement. The superiority of the latter is so great, however, that manufacturers are finding it pays them better to take more pains to secure a uniform product of a composition and properties practically identical with those of Portland cement. Some of them have, therefore, installed arrangements for testing and adjusting the composition of the raw material and of treating it in the same manner as in making Portland cement. The process is certainly more costly, but the better prices obtained fully warrant the additional expense. With natural materials so nearly correct in composition, it seems unfortunate that firms should continue to produce so inferior a product as natural cement when they might so advantageously manufacture Portland cement. To do this, it is essential that the materials should be ground to powder, its composition adjusted and the powder thoroughly mixed before it enters the kiln.*

Roman cement is one of the oldest of the natural cements, but its name is misleading as it bears no resemblance to the mortar used by the ancient Romans. It was first made in England in 1796 by burning clayey nodules found on certain parts of the sea coast.

Rosendale cement is a natural cement made from an argillaceous magnesian limestone which occurs in the Appalachian range. It differs from most other natural cements in containing 15 to 18 per cent of magnesia.

Grappier cement is made by grinding the lumps obtained as a residue when hydraulic limes are screened. It may be regarded as a natural cement occurring in a hydraulic lime. The best specimens have a composition very similar to Portland cement, but the composition varies greatly with different samples.

All the foregoing cements are characterized by a high-binding power, as a result of which they may be mixed with several times their volume of inert material such as sand, the product being a plastic paste which may be made into articles of any desired shape by modeling, molding, compression or extrusion. In a short time, the mass loses its plasticity and is then said to *set*, after which it gradually hardens until it forms an artificial stone.

* Much of the Belgian cement imported into the United States is a natural cement.

Sand cement is a mixture of Portland cement and finely-ground sand. It has higher compressive and tensile strengths than most cement and is sometimes sold as a substitute. Its true nature is readily shown by mixing it with three parts of standard sand as the product is much weaker than that of a true Portland cement. The reason that sand cement gives higher strength-tests is that in neat cement the strength is not fully developed, some of the cement behaving as an inert material. When mixed with a suitable proportion of sand, however, the full strength of the cement is used.

(2) *Pozzuolanas* are not true cements, but only become so when mixed with lime and water. The raw materials composing pozzuolanas are, essentially, clays which have been heated to redness either by natural forces, such as volcanic action, or artificially in kilns. Pozzuolanas are, as regards their origin, of three classes:

(*a*) The direct products of volcanic action usually found on the slopes of volcanoes, such as pozzuolana proper, santorin, tosca, tetin and trass. These pozzuolanas bear a close resemblance to ashes and slags.

(*b*) Products of the decomposition of certain igneous rocks. These are feeble hydraulites.

(*c*) Artificial pozzuolanas obtained by crushing lightly-burned clay, ballast, tiles, bricks, etc. Care should be taken to avoid clays which have been heated to partial vitrification. Some blast- and steel-furnace slags, when ground, are also pozzuolanic and when mixed with hydrated lime will form cements.

Very finely ground pozzuolana—either natural or artificial—is a valuable addition to Portland cement as it readily combines with the lime set free when the cement is mixed with water forming an additional quantity of cementitious matter. If the pozzuolana is coarsely ground, it remains inert and useless.

Cements made by mixing lime and pozzuolana are very slow-setting and of only moderate strength. They are, therefore, inferior to Portland cement and to many natural cements. The addition of pozzuolana to Portland cement or mortar is, however, an advantage, as it increases the cementitious value of these materials. In the case of Portland cement, it serves a still more important purpose, viz., to render insoluble the lime set free by the action of water on the cement. When no pozzuolana or its equivalent is present, the free lime may be washed out of the cement or concrete, leaving the latter porous and more readily attacked by the weather, etc.

The preparation and use of artificial pozzuolana from lightly calcined clay has not met with the appreciation it deserves. This is probably due to the fact that no firm with sufficient commercial ability has attempted its production on a sufficiently large scale. Yet the enormous strength of many ancient mortars appears to be certainly due to the presence of finely-ground calcined clay (potsherds). The clay, when burned, is converted into a crude pozzuolana which—if the product is sufficiently finely-ground—can combine with the lime set free when the cement is mixed with water. In this way, a small excess of clay is an advantage as it adds slightly to the strength of the cement. Unfortunately, the natural products are usually coarsely ground, and when that is the case, the pozzuolanic effects cannot be developed.

(3) *Hydraulic limes* are mode by heating argillaceous limestones (i.e. limestones containing a considerable proportion of clay and silica). They differ from the siliceous cements inasmuch as they do not undergo any fusion and also in containing a large excess of free lime. Hydraulic limes may, in fact, be regarded as intimate mixtures of Portland cement and free lime in variable proportions.

(4) *Aluminous cements* are comparatively new, the most important are

ciment fondu, ciment électrique, aluminous cement, "alca" cement, fused cement, etc., which have been in extensive use for only about twenty years, but their greatly increased employment during the War and since has drawn still more attention to their many advantages.

Blanchet [4] classifies the aluminous cements into three groups:

(*a*) *The pseudo-aluminous cements* which are merely imitations and not truly aluminous, being chiefly composed of calcium silicates with some calcium aluminate. They are of two kinds: (1) Portland or natural cements which have been carefully prepared so as to harden rapidly, and (2) some of the so-called "Belgian aluminous cements," which are made by adding bauxite and lime to basic slag. These cements contain only about 50 per cent of hydraulite and are weak.

(*b*) *Melilitic cements* which have been sintered but not fused. They consist mainly of monocalcium aluminate and dicalcium aluminosilicate and contain only about 53 per cent of hydraulite.

(*c*) *True aluminous cements* which have been fused. They consist mainly of monocalcium aluminate and contain about 72 per cent of hydraulite. The tendency to rapid setting of any pentacalcium trialuminate, $5CaO.3Al_2O_3$, present is stopped by the preponderance of monocalcium aluminate and a little calcium silicate which is also present. They are not Portland cements (which must be considered as being composed of silicates of high lime content with the tricalcium aluminate as a minor constituent), but are highly aluminous lime aluminates (mainly $CaO.Al_2O_3$ with some $3CaO.5Al_2O_3$ and with a small proportion of calcium silicate or silico-aluminates as minor constituents). This class of cement has been under investigation for a number of years by the U. S. Bureau of Standards [5] and by other investigators.

Theoretically, a pure aluminous cement should contain 35.45 per cent of lime and 64.55 per cent of alumina, but the commercial aluminous cements vary in composition within moderately wide limits, e.g. 30 to 45 per cent of alumina, 35 to 45 per cent of lime, 5 to 12 per cent of silica and 5 to 12 per cent of ferric oxide, with an average of 40 per cent alumina, 40 per cent lime, 10 per cent silica and 10 per cent ferric oxide. This corresponds to $5CaO.Al_2O_3$ and not to the monocalcium aluminate ($CaO.Al_2O_3$) which is usually presumed to be the chief constituent. According to Feret,[6] the best composition is: alumina 45 to 70 per cent, lime 28 to 47 per cent and silica less than 12 per cent, but he points out that even a small proportion of impurity may make necessary a large change in composition.

Iron compounds in a reducing atmosphere act as fluxes, but at fusion temperatures alumina readily replaces iron oxides and leaves them free and able to retard the setting. For this reason, an oxidizing atmosphere should be used in burning the clinker. Dyckerhoff has shown that aluminous cements need not be completely fused, but must be well-sintered.

The sudden quenching of the fused clinker will yield a glass or solid solution, and if the constituents are hydraulic, the internal stored energy of the vitreous system will be added to the energy of the setting, with the result that the reaction proceeds too rapidly and the surface hardens before the water has penetrated the interior. Manufacturers, therefore, cool aluminous cements so as to produce hydraulic material in a metastable crystalline state, as this gives a normal setting with a rapid hardening. There seems to be little reason to doubt that the essential constituent is monocalcium aluminate ($CaO.Al_2O_3$).

No free lime is liberated on setting, so that highly aluminous cements are not affected by sulfates; these cements are, therefore, highly resistant to sea-water and various "chemical" solutions.

The chief advantages of fused (aluminous) cements over ordinary Portland cement are (1) slow setting, but rapid hardening; (2) greater ultimate strength; (3) development of sufficient heat during setting to enable the cement to be used in frosty weather; * (4) greater resistance to sea-water. These properties also mean that (a) less cement can be used; (b) less shuttering is necessary, and (c) less time for storage is required. In addition, aluminous cements are not attacked by sugar juices or other liquids containing *sugar,* nor by coke, coal and ashes containing *sulfides* or *sulfates.*

Contrary to what is often stated, the chief advantage of aluminous cements (*ciment fondu*) is not in their rapid hardening—which is equally characteristic of some Portland cements—but in their extraordinary resistance to chemical action.

Since highly aluminous cements have become popular on account of their rapid hardening, there have been placed on the market, Portland cements, which also possess this property mainly as a result of finer grinding and minor differences in manufacture (*see under* Rapid-hardening Cements).

Attempts to make completely fused clinker of the same composition as Portland cements, have not been satisfactory. Such fused clinker does not produce a better cement—in most cases the fused material is inferior to ordinary Portland cement. Some of the Belgian aluminous cements appear to have been burned insufficiently and are, therefore, unsatisfactory in use.

(5) Some *plasters* may be termed cements; they consist of gypsum, which when partially dehydrated, forms plaster of Paris. This material when treated with water sets and hardens like other cements, though the process is probably much simpler as there is only one main constituent. The properties of the plaster of Paris may be modified by the addition of alum, etc., as in *Keene's cement.*

(6) *Oxy-acid cements* are quite different from the cements previously mentioned and consist essentially of a highly basic salt such as magnesium oxychloride or zinc oxyphosphate. The constitution of the oxy-acid cements is better known than that of the siliceous cements.

The magnesia is burned at about 800° to 900° C. in Europe, but at 1,000°-1,100° C. in the United States; if overheated, it becomes much denser and does not react so readily with the magnesium chloride, so that a much weaker cement is produced. The magnesium chloride is usually obtained as a by-product from the manufacture of potassium salts or from sea-water; it is used in the form of concentrated solution (sp. gr. 1·16—1·26).

The most important oxychloride cement is that known as *Sorel cement* † which corresponds in composition to $MgCl_2.5MgO.17H_2O$.

The constitution of magnesium oxychloride cements has been considered from the point of view of the stability relations of the system $MgO—MgCl_2—H_2O$ at 50° C. by Maeda and Yamane.[7] With solutions containing 14.01 per cent of magnesium chloride the solid phases $MgO.H_2O$ and $3MgO.MgCl_2.12H_2O$ co-exist in equilibrium with the liquid phase, whilst with solutions containing 37 per cent of magnesium chloride the double salt and $MgCl_2.6H_2O$ form the solid phases. $MgO.H_2O$ can remain in unstable equilibrium with solutions containing 14 to 21 per cent of magnesium chloride, above which only the double salt exists. With weaker solutions, the double salt decomposes.

* Some aluminous cements made in the United States do not appear to show any marked evolution of heat during the setting.

† The term *Sorel Cement* was originally applied to a zinc oxychloride cement invented by S. T. Sorel in 1855, but the term has for some years been applied almost exclusively to a magnesium oxychloride cement of analogous constitution, also discovered by Sorel, who found that the oxychlorides of iron, manganese, nickel and cobalt can be prepared in a similar manner and used as cements.

From these data, ordinary Sorel cement appears to consist of the double salt ($3MgO.MgCl_2.12H_2O$), monohydrated magnesium oxide ($MgO.H_2O$) and solution, the proportion (57 to 62%) of double salt is fairly constant, but the other two constituents vary within wide limits.

According to Maeda,[8] the setting of magnesium chloride cements is due to the liquid phase becoming supersaturated with the solid which crystallizes out in small aggregates on which water is later adsorbed. This is confirmed by Feitknecht,[9] who has shown that in order that setting may occur, the concentration of the magnesium chloride must be sufficient, though with too concentrated a solution the hardness of the cement increases rapidly at first and then more slowly. He has also shown that, provided it is sufficient, the smaller the proportion of water used the harder will be the cement when set.

Maeda [10] has suggested that hardening is a continuation of the setting process and is due to the formation of the double salt $3MgO.MgCl_2.12H_2O$. During the hardening it is necessary for sufficient water to be present; otherwise brittle cements will be formed. If this is correct, free water is necessary, first for plasticity and then for crystallization and subsequent adsorption.

It is generally agreed that the setting is not due to the formation of oxychlorides, but to the crystalline grains growing or swelling until they cohere.

That some kind of colloidal change occurs appears to be shown by the increase in the volume of mixtures of magnesia and sawdust (3:1) with sufficient solution of magnesium chloride (sp. gr. 1·16) to produce a suitable paste. These changes in volume after various periods depends [11] on the reactivity of the caustic magnesia and on the conditions of humidity to which the mixture is exposed. The volume, loss of moisture and change in strength increase during the first four weeks and then remain constant.

Grün,[12] however, attributes the setting to the formation of colloidal magnesium hydroxide and not to crystals of oxychloride.

Without going into further details it appears to be fairly certain [13] that both crystals and the colloidal matter are formed and that in any full explanation of all the phenomena of setting and hardening both these states of matter must be included.*

Magnesium oxychloride cements are among the strongest cements known. A mixture of 1 part of such cement with 4 parts of sea sand gives a crushing strength of over 8,000 lb. per sq. in. One part of the oxychloride will serve to cement 8 parts of sand. The cement is not appreciably affected by exposure to frost, rain or occasional flooding, and, therefore, finds extensive application in the manufacture of artificial stones used for building purposes, especially window sills and door-steps, but it is not suitable for stones constantly exposed to water. Instead of sand, sawdust is sometimes used for floors and interior walls.

Zinc oxychloride cement is made by mixing equal volumes of dense (highly calcined) zinc oxide with a syrupy solution of zinc chloride (sp. gr. 1·53—1·71 or 50° to 60° Bé), containing about 3 per cent of borax or ammonium chloride which acts as a retarder.

Most oxy-acid cements differ from Portland and similar cements in having a low binding power. They cannot, usually, be mixed with relatively large quantities of inert material, but must be used alone when required as fillers or in the production of plastic masses or for articles of any particular shape.

(7) *Fire-cements* or *refractory cements* usually consist of fire-clay made into a paste with water. They are chiefly used instead of mortar in construct-

* The colloidal matter probably contains *crystals of colloidal dimensions*, which do not act like larger crystals. Crystallinity and colloidality are not essentially incompatible terms. J. A.

ing the linings and arches of furnaces and kilns. The fire-clay is hardened as the structure is heated and so binds the bricks together. Mortar could not be used for this purpose, as, at the high temperatures attained the lime and sand would combine and form a molten slag, part of which would run out of the joints, whilst the remainder would attack the brickwork.

During the past few years, considerable improvements have been made in fire-cements. The excessive shrinkage of plastic clay has been reduced by using a mixture of clay and silica powder or grog (which is equally resistant to heat), and greater strength at all except the highest temperatures has been attained by using a mixture of fire-clay, silica or grog, and Portland cement, water-glass or similar binder. Such additions reduce the ultimate heat-resistance of the material, but this is of no importance when the furnace is worked at a temperature far below the refractoriness-point. Portland cement and similar cements are not really fire-proof. All concrete made with them fails if heated for a long time at 700° C. and may fail at a much lower temperature.

Organic Cements

These cements are so numerous and many of them are so complex that it is difficult to arrange them in any satisfactory grouping. They may, however, be classified as:

(*a*) Organic cements which are applied to solid substances in order to unite the latter, as when two pieces of wood are glued together by casein, fish-glue, animal glue, etc.

(*b*) Organic cements which are mixed with non-cementitious material in order to produce a mass possessing plastic properties and, therefore, capable of being molded or otherwise given any desired shape.

Mortar

Mortar may be regarded as a mixture of a cement or binding agent with an inert material or aggregate, the product being plastic and capable of being given any desired shape whilst fresh, but in course of time, it loses its plasticity and gradually hardens and forms a stony or rock-like mass. Mortars are of various kinds, the most important being:

(1) *Lime mortar* or ordinary builder's mortar which is composed of 1 measure of fat lime and 2 to 4 measures of sand, but hair, dung and other fibrous materials are sometimes added to act as a reinforcement. Ashes and other waste materials of an inert nature are sometimes used to replace the sand, where such materials are sufficiently cheap. The "fat" lime is almost pure calcium oxide or a mixture of calcium and magnesium oxides.

When a stronger mortar is required, one of the following is used, some or all of the lime being replaced by Portland cement or other materials.

(2) *Hydraulic lime mortar,* which is made of hydraulic lime and sand. Such mortar is preferable to mortar made from fat lime as hydraulic lime is more cementitious and is not so readily removed when the mortar is subjected to the action of water. As explained later, hydraulic lime really consists of two ingredients—cement and free lime; the former behaves very much like Portland cement and the latter like fat lime in ordinary mortar. Hence, hydraulic lime combines the advantages and defects of both its constituents; its hardening is not solely confined to the surface, as with lime mortar, and yet it does not harden so completely as cement-mortar, because of the excess of free lime present. (See also *infra* with respect to the effect of adding lime to cement.)

(3) *Trass mortar* is made by mixing fat lime and trass or its equivalent,* so that these materials will combine in suitable proportions, and then adding sand according to the strength which the resultant mortar must possess. In this case, the sand is a diluent added for cheapness; the larger the proportion of sand, the weaker will be the mortar. The precise proportions of trass and lime which will give the best results must be found by trial as they depend on the activity of the trass and lime employed. In a large number of samples examined by the author, the average optimum proportions are one measure of hydrated high-calcium lime, one and one-half measures of trass and two measures of sand where the mortar is to be continuously exposed to water, but for quays, damp-proof courses and ordinary foundations, three or even five measures of sand may be used so as to reduce the shrinkage as well as the cost of the mortar. An excess of trass does no harm, as it merely acts like fine sand, but an excess of lime is objectionable in mortar which may be exposed to the action of water. There is little or no advantage in using hydraulic lime in conjunction with trass. A properly proportioned trass-lime mortar is one of the most water-proof mortars which can be made.

(4) *Cement mortar* is a mixture of Portland (or natural) cement and sand, usually in the ratio of 1:3, but cheaper mortars consisting of 1 part of cement to 6 of sand are sometimes used. For work which is required to be completely water-proof, not more than 2 parts of sand may usually be employed, but such a mixture shrinks too much if exposed to the air and so gives unsatisfactory results.

Portland cement, when purchased, is devoid of free lime, but after mixing with water, lime is set free and will, eventually, be washed out of the joints if the masonry or brickwork is exposed to water. This is the explanation of most of the white patches on concrete and grouted cement work. The spaces left when the lime is removed leave the mortar porous so that it is not water-proof. To overcome this objection, some substance such as pozzuolana, trass or brick-dust must be added to combine with the lime and to render it insoluble. For this purpose, rather more trass than cement should be used. A mixture which is very generally suitable consists of 1 measure of trass or equivalent, 1 of Portland cement and 2½ to 3 measures of sand.

(5) *Lime-cement mortar* is made by mixing lime, Portland cement and sand. The addition of the lime increases the mobility of the mortar, so that it is easier to use, but the effect of the lime on the stability of the mortar is often harmful. A little consideration will show that if the lime liberated from the cement and washed out by percolating water is sufficient to make the mortar porous, any additional lime will only increase the damage.

A 1:2 cement: mortar for waterproof work is a very costly mortar, so that it is usually replaced by one measure of cement, one measure of lime-powder and three measures of sand. Many masons find 1:3 cement: mortar difficult to work, but by adding half a part of lime-powder the difficulty disappears, so that one measure of cement, half a measure of lime and three to four measures of sand is a very usual mixture, though still too costly for many builders. More lime is, therefore, added, and a mortar compound of one measure of cement, two measures of lime-powder and ten to twelve measures of sand is found to work well but the more the lime exceeds the cement, the more does it hinder the hardening of the latter, the damper the walls will remain and the more readily will water percolate through the material.

* For the sake of brevity, only the term trass is used, but the reader will understand that these remarks will apply with equal force to mortars rontaining other hydraulic agents—pozzuolana, santorin earth, crushed bricks, slag-meal, etc.

It is a curious fact, for which no satisfactory explanation has yet been published, that when lime-cement mortar is used, efflorescence or wall-white sometimes appears only after the building has been completed for a considerable time. This is the more unfortunate, because the architect or builder leaves the work in an apparently good condition. The slowness with which this defect becomes visible may explain why most builders persistently continue to use mortars which are unsatisfactory, but do not have this defect.

(6) *Trass-cement mortar* consists of a mixture of trass or its equivalent with Portland cement and sand. The trass is added to combine with the lime and make it insoluble as described above. Hence, the advantage of adding a suitable quantity of trass is two-fold:

(*a*) it fixes the lime and prevents the defects caused by its removal;

(*b*) the compound thus formed increases the strength of the mortar by its own cementitious power, i.e. by converting the useless free lime into a useful cement. It therefore follows that the addition of a suitable proportion of trass will enable a somewhat smaller proportion of Portland cement to be used and a saving to be effected in the cost of the mortar.

Also, when for want of a better material, a builder is forced to employ a cement of such low quality that it will not pass the usual official tests for durability—such as some natural cements and hydraulic limes—the most serious consequences may be avoided by adding a suitable quantity of trass to the mortar or, preferably, by grinding the trass with the cement so that both are of the same fineness.

The amount of trass to be added depends on the nature of the work. Some cements when ground with half a measure of trass, give higher results in tensile and crushing strengths than those without trass. By the addition of trass, the hardening is delayed; in some cases this is an advantage, but in others it is inconvenient. Any increase in the strength of the masonry is of no interest; in the case of concrete it is sufficient to know that the strength is not reduced by trass.

The minimum amount of trass to be added may be calculated if the composition of it and of the Portland cement are known. It is that amount which will combine with the lime liberated by the cement during setting and hardening. With the best Rhenish trass the smallest quantity which will unite with the lime set free by Portland cement of average composition is 0·4 lb. of trass for each 1 lb. of Portland cement used. This assumes that the trass has been ground as fine as the cement and that the two have been perfectly mixed. In actual work, it is necessary to use at least half as much trass as Portland cement. As an excess of trass does no harm, a larger proportion than that mentioned is generally advisable.

Mortar composed of one measure of cement, half a measure of trass, and three measures of sand has proved, in practice, to be very good to work; that composed of one measure of cement, one measure of trass and four or even five measures of sand is equally good; even with a 1 : 1 : 5 mortar, willing workmen have executed plastering without difficulty.

For general purposes, the proportion given above (viz., equal volumes of Portland cement and trass) is good, but where a more rapid hardening and a greater strength are required, the proportion of trass must be reduced to one-half or one-third. For masonry and brickwork exposed to water, trass or its equivalent should never be omitted.

(7) *Clay-mortar* is seldom employed, except for furnaces and other structures to be used at high temperatures. As the clay shrinks greatly when heated, it should be mixed with sufficient silica or grog to reduce its shrinkage

to suitable limits, or a lean clay with a shrinkage not exceeding 1 in. per linear foot of mortar must be substituted. The addition of a little tar or oil enables a larger proportion of sand or brick dust (grog) to be used than when water is employed to produce a paste.

Clay-mortar is excellent for setting bricks and for much interior work which is not required to resist the action of the weather.

Many builders make the curious mistake of thinking that a mortar rich in clay is necessarily superior to one rich in sand. Precisely the contrary is often the case.

Where avoidance of shrinkage is of great importance, it can be secured more certainly with clay mortar than with any other.

The *chemical constitution* of mortars is, at first, that of a simple mixture, but is quickly changes because of the reactions which occur between the various constituents. These changes are described later.

Changes Which Occur in Manufacturing Portland and Other Cements

It is doubtful whether any changes of importance occur during the mixing of the various ingredients, though prolonged grinding with water must certainly facilitate several minor reactions.

In the burning process, the formation of the "clinker" which when ground, is known as Portland cement, is an interesting example of a series of reactions which occur in a mixture of solid materials whose temperature is gradually increased until partial fusion occurs. The rise in temperature, even under "ideal" conditions is not uniform. At about 400° C. there is a "halt" due to the decomposition of any clay present; at about 910° C. there is a second "halt" due to the dissociation of the calcium carbonate (limestone). A positive evolution of heat (exothermic reaction) also occurs at temperatures corresponding to the formation of calcium orthosilicate, $2CaO.SiO_2$, and monocalcium aluminate, $CaO.Al_2O_3$, but at 1,285° C. an absorption of heat (endothermic reaction) occurs due to the formation of fused material and probably of a eutectic. Above this temperature, no characteristic changes occur in the heating curve.[14] On cooling, a "halt" in the curve at 1,215° C. indicates the solidification of an important eutectic. Other minor changes occur in the heating curve, but their significance is not well understood. As fusion is never complete and the temperature is rising throughout the whole period of burning, there can be no true equilibrium; the reactions are arrested before many of them are complete.

Under such conditions there is almost certain to be an indefinite amount of *colloidal* matter formed, but it is impossible in the present state of knowledge to estimate its amount or to do more than guess at its nature and properies. It is easier to understand what occurs when producing cement clinker, if the colloidal properties are disregarded and the various changes are considered to be the result of definite chemical reactions associated with a series of solutions in a sintered or partially vitrified material, with the formation of some eutectics. The formation of a suitable melt is only necessary in order to produce, at a suitable temperature, a fluid in which the stabilization of the mass may occur on cooling and the absorption of the lime may take place.

The cold clinker and the ground cement are both devoid of colloidal particles so far as any definite proof of colloidality is concerned, though it is possible that free lime is dispersed in a colloidal state in the clinker or in one of its constituents.

The chemical constitution of Portland cements and analogous materials is still uncertain, there being three widely different groups of theories:

(*a*) That associated with the names of Le Chatelier, Tornebohm, Keisermann, Michaelis [15] and others who claim to have found four groups of substances known (for want of better names) as *alite, belite, celite* and *felite*. The composition of these groups is still uncertain.

The early view, that *alite* is chiefly composed of $3CaO.SiO_2$ is not now held, it being generally understood that this substance is a solution of lime in the β-di-silicate, i.e. the formula should not be $3CaO.SiO_2$, but $2CaO.SiO_2 + CaO$. This conclusion, primarily due to Dyckerhoff,[14] has been confirmed by other investigators working on commercial cements, but is not accepted by all. Several investigators still maintain that alite is essentially composed of $3CaO.SiO_2$ or of mixed crystals of $3CaO.SiO_2$ and $3CaO.Al_2O_3$,[16] but Jänecke [17] declares that this is incompatible with the different properties of these two compounds and reiterates his belief in jäneckite (*vide infra*). Harrington [18] found zonal structure in the alite crystals which, he claims, shows that they are mixed crystals. Kühl [19] considers it to be composed of mixed crystals of jäneckite (see *c*) and $3CaO.Al_2O_3$ or $3CaO.SiO_2$. Shimizu[20] finds that this corresponds to the electrical conductivity-time curve of Portland cement.

E. Martin[21] has found that if a mixture of one mol of silica and two mols of calcium carbonate is heated at 1,200° C. and the free lime removed with a solution of sugar, the residue corresponds to $10CaO.5SiO_2$ and is inactive as a cement. It is completely soluble in acetic acid and sodium carbonate removes 3 mols of silica from it. Martin also found that if one mol of silica is heated with 3 mols of calcium carbonate at 1,400° C. the product is a cement. It is completely soluble in acetic acid. When it sets, $3Ca(OH)_2$ is liberated and $10CaO.5SiO_2.2H_2O$ is formed, but the latter undergoes further hydrolysis.

Belite is a dirty green color, probably due to absorbed iron. It has not been isolated in a sufficiently pure state for analysis, but appears to be an impure form of *calcium orthosilicate*, $2CaO.SiO_2$, though Le Chatelier [15] regards it as *tricalcium aluminate*, $3CaO.Al_2O_3$.

Celite is a flux or glassy material of a deep brownish orange color. It appears to be an impure solution of $2CaO.Al_2O_3$ in $2CaO.SiO_2$, but Le Chatelier [15] gave it the (assumed) formula of $3CaO.2(AlFe)_2O_3$, though Campbell [22] regards celite as a definite compound, viz., $5CaO.3Al_2O_3$, whilst Kühl [19] regards it as a variable mixture of dicalcium ferrite and $4CaO.Al_2O_3.Fe_2O_3$. It has not been sufficiently well isolated for its nature to be accurately known.

Felite forms colorless crystals in some decomposed slags; its composition is not accurately known but Kappen and others regard it as a non-hydraulic form of calcium orthosilicate, possibly $\gamma 2CaO.SiO_2$, with some magnesium orthosilicate.

According to Dyckerhoff, it is not yet possible to make any reliable statements about belite, celite and felite as the system lime-alumina-iron oxide-silica has not been fully explored.

The problem is complicated by the fact [23] that cements made by mixing pure tricalcium aluminate, tricalcium silicate and β-dicalcium silicate have a lower tensile strength than commercial Portland cements at various ages. This may be due to the beneficial effects of impurities in the commercial cements.

(*b*) Rankin and others [24] have concluded, from a consideration of the lime-alumina-silica system made of synthetic mixtures, that the chief components

are $3CaO.SiO_2$, $2CaO.SiO_2$ and $3CaO.Al_2O_3$, but *not* the $5CaO.Al_2O_3$ found in commercial cements. Day, Shepherd, Rankin and Wright [25] have found that specimens which were thought to be the synthetic trisilicate were really composed of an intimate mixture of lime and calcium ortho-silicate crystals, which may easily be mistaken for a homogeneous substance. On the other hand, Bates and Klein [26] claim to have prepared tricalcium silicate of a purity of 95 per cent, and to have found that its properties are precisely the same as Portland cement. They also found that a mixture of finely ground tricalcium silicate, tricalcium aluminate and dicalcium silicate in suitable proportions also had the same properties, but that a mixture containing too much dicalcium silicate hardened too slowly to be of use, and one containing too much tricalcium aluminate set much too rapidly and attained too little strength.* They concluded, like Rankin, that Portland cement is a mixture of tricalcium silicate, tricalcium aluminate and dicalcium silicate, and does not consist chiefly of an aluminosilicate.

Bates and Klein [26] found that a synthetic cement, made of $3CaO.Al_2O_3$ only, set much too rapidly and attained too little strength to be commercially useful, and that synthetic mixtures of this aluminate with tricalcium silicate containing more aluminate than normal cements, had the same defect.

Micro-sections [27] show the resorption of the primary tricalcium silicate through fusion and the formation of $2CaO.SiO_2$ in equilibrium with $3CaO.Al_2O_3$, but X-ray spectrograms show the simultaneous existence of both di- and trisilicates, the aluminate, and free lime in the fused portion.

Campbell [22] doubts the existence of $3CaO.Al_2O_3$ and regards it as a solution of lime in $5CaO.3Al_2O_3$. Shimizu [20] found that the break corresponding to the calcium aluminate does not appear in the conductivity-time curve of Portland cement which it should do if Rankin's deductions concerning the constitution of Portland cement, viz., that its composition is approximately $3CaO.SiO_2$, 45 per cent; $2CaO.SiO_2$, 35 per cent; and $3CaO.Al_2O_3$, 20 per cent, are correct. On the other hand, it is stated by the officials of the United States Bureau of Standards [28] that $3CaO.Al_2O_3$ is the only aluminate present in normal cement.

(*c*) That associated with the names of Dyckerhoff and others,[29] who suggest that the main constituent is β-$2CaO.SiO_2$ which absorbs lime in various proportions with some $5CaO.3Al_2O_3$ as a minor constituent. Dyckerhoff is of opinion that β-$2CaO.SiO_2$ is the source of the hardening power of the cement as this silicate is readily attacked by water whilst the γ-form is scarcely affected. The latter appears to be formed in the presence of much fused matter (glass), but less easily in the presence of alumina. According to Dyckerhoff, the β-$2CaO.SiO_2$ is stabilized by dissolving lime and so does not ordinarily invert into the γ-form. This is confirmed by Beckmann.[30] Dyckerhoff's investigations also show the great stability of some apparently unstable silicates when they are embedded in a eutectic melt. They are then difficult to convert into another form, but unless so embedded, decomposition occurs. It is theoretically possible for a calcium metasilicate to be present at all temperatures, but Dyckerhoff has shown that the time-temperature graphs of mixtures of lime and silica corresponding respectively to the orthosilicate and the metasilicate, are identical and that whatever proportions of lime and silica are used, the orthosilicate is produced. On heating to 1,400° C., it is suddenly converted into the metasilicate ($CaO.SiO_2$) and above this temperature only the latter exists.

* The possibilities of *multiple or cumulative colloidal protection* must be considered here. See Vol. 1 of this series. J. A.

(*d*) Jänecke[31] claims to have discovered the existence of $8CaO.Al_2O_3.2SiO_2$ which he named *jäneckite* (m. p. 1,382° C.) as the essential constituent of Portland cement (*alite*), but later investigators regard it as a eutectic or as a complex crystalline mixture and not a definite chemical compound. Jänecke has shown, however, that the lime in jäneckite can be replaced by barium oxide or strontium oxide and by using the X-ray method of Bogue and others,[27] he has confirmed the fact that a mixture of pure oxides of the same composition as jäneckite behaves like a mixture of lime, $3CaO.Al_2O_3$ and β-$2CaO.SiO_2$; he explains this as a complex isomorphism between jäneckite and β-$2CaO.SiO_2$. Shimizu[20] states that the electrical conductivity-time curve indicates the presence of jäneckite and no free calcium aluminate.

According to Dyckerhoff,[29] jäneckite is not formed below about 1,800° C. and as the clinker of which Portland cement is made does not reach this temperature, jäneckite cannot occur in normal Portland cement but only in clinker which has been seriously overheated. Dyckerhoff obtained characteristic crystals of jäneckite by completely fusing normal Portland cement in an oxyhydrogen flame and allowing the mass to cool slowly. In other words, he regards it as a product of over-heating and not of the normal burning of cement.

A comparison of these theories and of the large number of other investigations which have been made, shows that there is so much divergence of opinion as to the chemical constitution of Portland cement, that no positive statements in simple terms can be made concerning it.

This uncertainty is largely due to the fact that the manufacture of Portland cement involves a series of "arrested reactions" the nature of which cannot be satisfactorily determined from equilibrium diagrams or from experiments with pure materials. The arresting of the reactions means that there can be no equilibrium. The solid particles dissolve at varying rates in the melt, they then enter into reaction, produce conditions of saturation for some substances which then crystallize out as new minerals. By the nature of the case there can be no equilibrium until fusion is complete, no matter how long the mass is held at one temperature. Hence, the preparation of the material and especially the size of the particles, have a marked effect, and it is easy to see how much the properties of the cement must depend on the duration of the heating as well as on the temperature and how important are the rates of heating and cooling. Practical men have long known that all these were important factors, but an adequate scientific explanation is lacking.

The question as to whether *free* lime exists in Portland cement is often asked. It does not exist in fresh, well-made modern Portland cements, but does occur in some badly made cements especially if they have been imperfectly burned. According to Kühl,[32] the action of the lime during the burning of the cement is as follows:

1. The calcium carbonate is converted into quicklime at 750° to 950° C.
2. Half the lime enters into combination by the time the last of the carbon dioxide has been expelled. The low lime compounds are formed first and the high lime compounds last.
3. Dicalcium silicate is chiefly formed between 1,000° and 1,250° C.
4. The occurrence of a liquid phase at about 1,250° C. causes a violent reaction in which lime is taken up and alite and celite formed. (Kühl regards alite as a variable mixture of $3CaO.Al_2O_3$ and jäneckite, or a hypothetical dicalcium aluminate and celite as a variable mixture of dicalcium ferrite and $4CaO.Al_2O_3.Fe_2O_3$.)
5. The quantities of lime which combine with the clay at 1,250° to 1,450° C. are of such a magnitude that Kühl considers that dicalcium silicate cannot be the principal constituent of Portland cement.

Rankin[33, 40] holds a different view; the changes which he considers take place on heating the mixed raw materials to form Portland cement are as shown in Table 2.

TABLE 2. *The Temperatures of Formation of the Constitution of Portland Cement.*

Raw Mix.	1,000° C.	1,000° to 1,335° C.	1,335° to 1,450° C.	1,450° to 1,650° C.
CaO Al_2O_3 SiO_2	CaO Al_2O_3 SiO_2	CaO $5CaO.3Al_2O_3$ $2CaO.Al_2O_3$ $3CaO.Al_2O_3$	CaO, Flux $3CaO.Al_2O_3$ $2CaO.SiO_2$ $3CaO.SiO_2$	$2CaO.SiO_2$ $3CaO.SiO_2$ $3CaO.Al_2O_3$

All the free lime present at 1,450° C. is combined (according to Rankin) or enters into solid solution (according to Dyckerhoff) at a slightly higher temperature. The impurities present lower the temperature at which the reactions occur (as compared with pure materials), but do not otherwise affect the result.

Tremmel[34] has determined how much lime can be absorbed by the systems lime-alumina-silica, lime-iron oxide and lime-iron oxide-silica, using White's reagent (phenol in nitrobenzol).[35] He found the silica-lime ratio varied from 1:2·52 to 1:2·96 and that in a *sintered* mixture it cannot exceed 1:2·65 (confirming Dyckerhoff) and that even on fusion this limit is retained. He found that $3Ca.SiO_2$ is formed under abnormal conditions and that it is accompanied by swelling and cracking in the pats of cement paste.

In the lime-iron oxide system the only compound is $2CaO.Fe_2O_3$. In the lime-iron oxide-silica system, half the $2CaO.Fe_2O_3$ serves as a flux whilst the other consists of SiO_2 and CaO in variable ratio 1:2·45 to 1:2·80. With a ratio above 1:2·60, free lime occurs.

An investigation of the constituents of aluminous cements leads to more definite results. The optical data of synthetic mixtures and the commercial cements agree so closely that the existence of the definite compounds revealed by a micro-petrographic investigation is assured.

These cements belong to the ternary system, lime-alumina-silica, and occupy a field near the aluminate $CaO.Al_2O_3$ which is also near that of the Portland cements.

Agde and Klemm[36] after examining such cements microscopically, reached the conclusion that they consist chiefly of a melilitic body in a glassy groundmass.

It is generally agreed that the chief constituents of fused aluminous cements are $CaO.Al_2O_3$ and $5CaO.3Al_2O_3$. The latter was found by Rankin and Wright[37] to be the most fusible of those formed when lime and alumina are heated to incipient fusion; it hardens rapidly but disintegrates quickly in water.

Dyckerhoff[38] has shown that in aluminous cements there is a large proportion of the unstable α-$5CaO.3Al_2O_3$ which he regards as the source of the hydraulic properties. Any $3CaO.Al_2O_3$ and β-$2CaO.Al_2O_3$ present appear to be of minor importance.

Shimizu[20] has observed that the specific electrical resistance of aluminous cements is much higher than that of Portland cement. He attributes this to the presence in the aluminous cements of tricalcium aluminate which is very reactive to water and sets very rapidly. The existence of $3CaO.Al_2O_3$ has been doubted by Campbell.

There appears to be an almost continuous series of cements between the

Portland cements and the aluminous cements which show great similarities in their hardening processes; this suggests that the same substances exist in all these cements though in very different proportions.

Have These Cements Colloidal Properties?

The colloidal nature of cements, such as Portland cement, is peculiarly difficult to investigate because they are so easily decomposed. They must, indeed, be regarded as potential colloids rather than as actual ones, because any colloid is necessarily composed of two substances or, more rarely, of one substance in two phases, whereas Portland cement and allied materials remain inactive until they have been mixed with water. In this sense, the two phases which are essential to an exhibition of colloidal properties are the cement and the water. The subject is made still more complex by the lack of knowledge of the constitution of the cement, for the cement itself may contain several substances in solid solution or in a dispersed state. Thus, the free lime supposed by Dyckerhoff and others to be in solution in a glassy dicalcium silicate may be, and not improbably is, in a colloidal state, the two substances forming a *gel.**

It was, at one time, regarded as sufficient to prove that a substance was amorphous in order that it might be classified as a colloid, but this is no longer the case, as some substances which possess marked colloidal properties (e.g. gold sols) have been found to be crystalline so far as the suspended matter is concerned. For this reason, it is becoming increasingly necessary to distinguish colloids from amorphous materials generally and to apply the term "colloidal" exclusively to substances which consist of particles of certain sizes and which have certain characteristic properties, i.e. the size of the particles and the existence of two phases—not their amorphousness—is the criterion as to whether they are in the colloidal state or not.

As is well-known, colloidal substances can exist in two forms: (1) as a *sol* in which the ultramicroscopical particles are suspended in a suitable liquid, and (2) as a *gel* in which the suspended particles in a sol have become coagulated or flocculated in such a manner as to produce a semi-solid, jelly-like or glassy material. Some gels are readily converted into sols, but in others the conversion is so slow or so difficult that they are described as "irreversible."

It is obvious the Portland cement and allied materials are not sols or gels in the ordinary sense of the term, and, except in a more obscure sense, they can scarcely be described as colloids. Sometimes the term *pyrocolloids* is applied to them, but the correctness of such an application is by no means established.

It is sometimes stated that the colloidal nature of a substance can be established by suspending its particles in a suitable liquid or dispersion medium. Whether this is true of Portland cement remains to be proved, for no suitable dispersing medium which does not decompose it has yet been found. Water, which would be most convenient, cannot be employed as it decomposes the cement. Measurements of the sizes of the particles of cement which pass through a 200-mesh sieve show that most of them are far too large to be regarded as "colloidal." Yet, as suggested above, they may be fragments of a pyro-gel and, therefore, truly colloidal. Unfortunately, the optical methods for recognizing the colloidality of glasses and other pyrogels are only applicable to semi-transparent or translucent materials and so cannot be applied to cement clinker. For the same reason, all the ordinary properties which are

* The term *Pyrosol* is applicable here. See paper by R. Lorenz in Vol. I of this series. J. A.

regarded as distinguishing colloidal substances cannot be demonstrated in Portland and allied cements without decomposing them. Any argument that such cements are colloidal in character must, therefore, be based largely on negative evidence and on analogy.* All that can certainly be said is that if Portland cement and allied materials are colloids, their colloidal properties cannot be recognized directly, so that even though they may form colloidal matter when mixed with water, it cannot be proved that such colloidal matter exists in the cement itself.

The same is true of hydraulic limes and the so-called natural cements which are equivalent to a Portland cement containing an indefinite quantity of the raw materials and of the products, such as lime, formed by the heating of some of these materials at a lower temperature than is required to produce Portland cement.

The Effect of Water on Cements

When Portland cement or an allied material is wetted, a chemical reaction occurs between it and the water, the former being decomposed. The course of the reaction is by no means simple and is greatly affected by the proportion of water added.

The complex physical and chemical phenomena which accompany the interaction of Portland cement and water are comprised under the terms *setting* and *hardening;* they occur in a series of characteristic steps.

On stirring a cement with water a stiff paste is produced which at first is no different from that produced with an inert substance such as sand. After a short time, however, a change is observable, the paste becomes plastic and increasingly resembles a paste made of plastic clay. Shortly afterwards, the mass becomes stiffer and eventually solidifies. The time taken to gain a prescribed amount of solidity (as determined by the depth of penetration of a Vicat's needle) is known as the *setting time.*

Cements which begin to solidify within a few minutes after mixing with water are described as *quick-setting;* those which require a longer time are termed *slow-setting.* Roman cements and hydraulic limes are usually quick-setting.

When a cement has set, it begins to *harden.* In many instances the hardening is merely a continuation of the changes which produced the setting, but in others a different set of phenomena occurs. The completion of the hardening requires a much longer time during which the cement becomes intensely hard and mechanically resistant. There is no definite period when the hardening can be said to cease. It increases somewhat rapidly at first, then more slowly afterwards, but specimens kept for several years are found to increase slightly in hardness and resistance to crushing the longer they are kept under favorable conditions. As the setting and hardening are obviously due to the action of the water, they are sometimes both included in the term *hydration.*

Each of the hydrated materials has a different index of refraction, so that if specimens after different times of hydration are ground and immersed in oil of refractive index 1·67 and counts of the particles are made some idea is obtained of the progress of the hydration and of the substances produced. The hydration is rapid at first, but soon slows down because of the ever-thickening envelope of hydrated gel.

The setting and hardening are accompanied by a rise in temperature, Portland cement rising 5° to 10° C. Aluminous cements, Roman cements and

* Some inferences as to the degree of dispersion may be drawn from X-ray spectrograms. J. A.

hydraulic lime show a greater rise. The electrical conductivity also changes, being highest shortly after the cement is mixed with water and gradually diminishes.

The period between the first addition of water and the loss of mobility is termed the *initial set.** With a quick-setting cement the change is very noticeable but with very slow-setting cements it is so indistinct as to be almost unrecognizable. In most cements, this division into two separate stages is strongly marked, but in plasters only one stage is observable.

Some modern rapid hardening cements show a *false set,* i.e. they appear to be set when the Vicat needle is applied, but if the mold is then rapped vigorously, the mass again becomes plastic and often an excess of water appears at the surface; afterwards the mass sets normally. By prolonging the mixing of the cement and water, the "false set" may be avoided. It is probably due to the greater fineness of modern cements, which makes the particles more difficult to wet with the normal amount of water. A false set occurs chiefly with a soft clinker which tends to clog and flake during grinding. The number of particles in a given volume of older and coarser cement is much smaller than that in a rapid-hardening cement and accounts largely for the difference in wetting of the two materials.

The proportion of water affects the time of setting, an excess of water retarding and too little increasing the rate of setting (see *Water-ratio, infra.*). An increase of temperature also increases the speed of setting and hardening. Hence, cements set more rapidly in hot climates than in cooler ones and some difficulty is often experienced in hot weather on account of the cement setting much more quickly than usual.

Various theories have been put forward to explain the setting of cements and the formation of a hard stony mass; the following are the principal actions which it is suggested may take place:

(*a*) The formation of a crystalline magma from a supersaturated solution.

(*b*) The formation of a colloidal gel.

(*c*) The reaction of various substances upon each other, or with water, giving rise to a product which is either crystalline, as in (*a*) or colloidal as in (*b*); the latter may afterwards be dissolved and later may become crystalline or the gel may enmesh any crystalline substances which may be found.

It will be seen that there are two entirely different explanations of the setting and hardening of cements—one depending upon crystallization from solution and the other on the formation of a colloidal gel—and a third theory which is a combination of the other two. The first two theories are apparently quite incompatible with each other, but in the light of recent research on colloidal phenomena it is possible that the difference is not so great as it might appear to be at first sight, and the third theory is now regarded as being the most acceptable.

Many years ago, it was considered that whilst crystalline substances are those having a definite geometrical form and produced by deposition from a supersaturated solution, colloidal gels, on the contrary, are amorphous,† had no definite geometrical shape, but on the gradual absorption of water they swell, the solid material being dispersed by the imbibed water, so that the whole mass passes from a solid jelly into a suspension of the solid matter in the liquid. The jelly is termed a *gel* and the suspension a *sol.* If the suspended matter is liquid instead of solid, an *emulsoid sol* is produced. Recent

* It is important not to continue adding water or to mix the materials after the initial set has commenced, or the interlocking network of particles will be destroyed.

† The amorphousness of the gel as a whole does not exclude the presence of finely dispersed *crystalline* particles.

advances in the study of colloidal phenomena have shown that some colloids may consist of definitely crystalline particles in suspension and so minute as to be invisible under the most powerful microscope, but if examined with an ultramicroscope they are found to be in a state of unordered oscillation termed the *Brownian Movement* after its discoverer (Robert Brown, 1827) and to possess definitely colloidal properties. Hence, it appears to be possible to have definitely crystalline particles in the colloidal state.

Before comparing these theories it is desirable to consider the action of water, separately, on each of the probable constituents of cements and afterwards to consider the mutual reactions of the various products on each other.

In the preceding section, it has been shown that the most probable constituents of cement clinker are *tricalcium aluminate,* $3CaO.Al_2O_3$, *tricalcium silicate,* $3CaO.SiO_2$, and *dicalcium silicate,* $2CaO.SiO_2$. The possible presence of compounds corresponding to $CaO.Al_2O_3$, $2CaO.Al_2O_3$, $5CaO.3Al_2O_3$, *jäneckite,* $8CaO.Al_2O_3.2SiO_2$, and free *lime* (*calcium hydrate,* CaO_2H_2) should also be considered. It is also desirable to take into account the theory that cement clinker may also consist largely of alumino-silicates.

The influence of impurities in the cements must not be overlooked. Some *iron compounds,* for example, can act as powerful fluxes and solvents and also as catalysts.

In examining these substances, it should be remembered that conclusions drawn from experiments on very small quantities of materials on a microscope slide must be used very discreetly, as such results are not necessarily analogous to those obtained in actual practice. For instance, it is well known that relatively small differences in the proportion of water used and the concentration of the salts present may make a great difference in the behavior of the cement.

Taking each of these materials in turn, the following data are important:

Tricalcium aluminate in the presence of water is hydrolyzed; according to Klein and Phillips,[39] it produces $3CaO.Al_2O_3.xH_2O$, the amount of water represented by x varying with the conditions. The product does not, however, develop great strength, nor does it readily disintegrate in water, though it is comparatively soluble.

Rankin [40] found that tricalcium aluminate sets and hardens very rapidly due to formation of an amorphous hydrate on the individual grains which are thus united. The amorphous materials sometimes crystallize. Slabs of this substance remain sound under water, but develop little strength.

A. J. Phillips [41] found that when tricalcium aluminate is treated with water a small proportion is dissolved and the remainder is partially hydrolyzed into an aluminate containing less lime and into calcium hydrate. The ratio of lime to alumina in the solution is not constant, but varies with time, the proportion of lime gradually increasing from 1·096 times the amount of alumina, after 3 hours, to 1·519 times after 28 days. It is possible that this variation is caused by the aluminate absorbing some of the lime set free and so altering the proportions from that of the original aluminate. In no case did Phillips find more than 0·6 gram of aluminate per liter in solution, so that it would appear that the solution has little to do with the hydration. The greater portion of the aluminate was found by Phillips to be in suspension in the water and he considers that it consists of a mixture of an emulsoid and a suspensoid colloid.

The suspension shows a distinct Tyndall effect; it can be dialyzed through parchment, does not diffuse into gelatin and when suspended in water containing a trace of sodium chloride and subjected to an electric current, migrates to the negative pole, thus showing that the particles are positively

charged. It is not coagulated by heat or alcohol, but by freezing. When dehydrated over sulfuric acid or by evaporation it does not form a gel, but a loose powder. In these respects, it resembles the sols of iron, aluminium and chromium hydroxides.

Bates [42] found that when tricalcium aluminate is soaked quietly in water, it is covered with a film which is but slightly permeable, so that hydration almost ceases. If, however, the material is agitated, the aluminate swells very considerably and becomes readily suspensible in water.

According to P. H. Bates and A. A. Klein,[43] tricalcium aluminate sets too rapidly and develops too little strength to be of use; but if it does not exceed 22 per cent of the weight of the cement it is useful in hastening the hardening and increasing the strength. They regard its function as doubtful.

Le Chatelier [15] states that when tricalcium aluminate is hydrated the product is apparently amorphous, but if a few isolated grains of aluminate are put into the water and then examined under the microscope, crystals may be observed to develop around the amorphous particles. Sometimes these crystals are large enough to be seen by the naked eye.

Phillips [41] has found that the presence of other substances has a profound influence on the behavior of colloidal tricalcium aluminate; thus, lime-water causes the amount of aluminate in suspension to be considerably increased, possibly due to the adsorption by the aluminate of positive Ca-ions. Phillips also found that the presence of plaster of Paris in the water used for suspending the aluminate, causes flocculation and precipitation to occur, though on increasing the proportion of plaster up to 3 per cent filtration was rendered easier. He considered this to be due to the sulfate present in an adsorbed condition being negatively charged. With larger amounts than 3 per cent, Phillips suggests that the adsorption of calcium ions by the aluminate overcomes the coagulating effect and increases the time required for the first set. Still further increases in the proportion of plaster again cause coagulation, and enable setting to take place more easily. The setting of the plaster itself also has an effect. He states that 15 per cent of gypsum causes a retardation of the setting. This is in accordance with the results obtained by Reibling [44] on the effect of gypsum on the setting of cements. He found that as the percentage of plaster is increased the set takes place first earlier, then later, and then earlier again, according to the proportion of plaster. If the aluminate crystallizes, Phillips considers that the sulfate would be less tenaciously held, as in the case of the retrograde adsorption of other colloids. This may, perhaps, account for the presence of gypsum crystals in hardened cements.

Bates [42] found that on the addition of hydrochloric acid to a suspension of tricalcium aluminate it rapidly coagulated to a solid mass; after some time, the watery phase gradually separated and solidified to a clear gel, containing both alumina and lime.

From the above results, it would appear that the setting of tricalcium aluminate is chiefly dependent on the formation and dessication of a colloidal material, the amount entering into solution being so small as to be practically negligible. Some crystallization occurs after a considerable time, but it does not appear to have anything to do with the first setting of the material. According to Rankin [40] it sets and hardens rapidly.

Bates and Klein [43] found that a synthetic cement, made of $3CaO.Al_2O_3$ only, set much too rapidly and attained too little strength to be commercially useful, and that synthetic mixtures of this aluminate with tricalcium silicate containing more aluminate than normal cements had the same defect. Camp-

bell[22] denies the existence of tricalcium aluminate in cement, and regards it as a solution of lime in $5CaO.3Al_2O_3$; the latter he regards as *celite*.

Dicalcium aluminate, $2CaO.Al_2O_3$, has been found by Newberry to be a quick-setting hydraulite with a constant volume and good hardening properties. Its presence in normal Portland cements is uncertain. Both tri- and dicalcium aluminate hydrolyze less in a solution of an aluminate than in plain water.[45]

The *pentacalcium aluminate*, $5CaO.3Al_2O_3$, is regarded by Campbell as *celite*. It readily hydrolyzes and sets very quickly, but it disintegrates when placed in water, as it is completely soluble. Klein and Phillips [39] found that, on hydrolysis, it liberates free colloidal hydrated alumina and forms colloidal tricalcium aluminate, which slowly crystallizes, the rate depending on the conditions. When the material is treated with steam, the formation of the crystals is accelerated. In an autoclave, still more of the crystalline product is formed, whilst on a microscope slide, the whole mass can be caused to crystallize. Klein and Phillips also found that, in the presence of lime-water, the liberated hydrated alumina reacts with the lime and produces tricalcium aluminate.

Monocalcium aluminate, $CaO.Al_2O_3$, on hydrolysis, liberates alumina and forms tricalcium aluminate which slowly crystallizes. The liberated alumina, which is colloidal, can combine with any free lime present forming more tricalcium aluminate. Under some conditions,[45] crystals of $CaO.Al_2O_3$ are formed with an increase in the pH value and in the molecular ratio $CaO : Al_2O_3$. If the solution of the aluminate is filtered to remove all insoluble matter and is stored, it slowly decomposes yielding the same products. On adding lime-water to the fresh mixture of aluminate and water the whole of the alumina is precipitated as monocalcium aluminate when the pH value exceeds 12.0.

Most aluminates react more rapidly with water than do the silicates and consequently play a more important part in the early stages of setting.

Tricalcium silicate, $3CaO.SiO_2$, when mixed with water, forms a gelatinous material which appears to be colloidal. It is doubtful to what extent the lime and silica remain combined or are dissociated. Klein and Phillips [39] suggest that calcium hydroxide crystals are produced together with an amorphous (colloidal) hydrated silicate, whilst Rankin [40] suggests that free colloidal silica may be liberated. He states that tricalcium silicate is the only one from which the silica is readily released, and suggests that colloidal silica is one of the principal cementing materials, if not the essential material in cements. Rankin found that tricalcium silicate hardened in water more rapidly than any other constituent of cement, and regarded it as the essential "hardening agent" though he admits that it cannot form more than one-third of the clinker. Klein and Phillips [39] found that tricalcium silicate alone hardens too rapidly and attains too little strength to be useful.

Dicalcium silicate, $2CaO.SiO_2$—the *ortho*silicate—occurs in three forms known respectively as the α-, β- and γ-forms. Of these, the α-form crystallizes in monoclinic prisms with a hardness of 5 to 6 on Moh's scale and is only stable above 1,410° C.; the β-form is produced when the α-form is cooled from 1,410° C. to about 675° C., and is orthorhombic with a specific gravity of 3.27; and the γ-form is produced by cooling to temperatures below 675° C.

According to Kühl,[32] the γ-form is the cause of "dusting" in cement which has been imperfectly burned, either through carelessness in controlling the kiln or in the use of an unsuitable mixture which is too low in alumina.

According to F. Hart,[46] the orthosilicate present in wetted Portland cement

does not separate as a gel in less than 24 hours, but can then be separated by decanting and washing with water. He found, on comparing the dehydration curve of the gel from a sample of "dusting" cement with that from a normal cement, that the former showed one "halt" at 35·69 per cent of water and a second "halt" at 31·27 per cent of water, indicating the presence of two different silicates or silicic acids, which he assumed to be orthosilicic acid and $2SiO_2.3H_2O$. This corresponds approximately to Dyckerhoff's γ-orthosilicate, but has a slightly different composition. The dehydration curve of the gel obtained from that part of the dusting cement which consisted of particles remaining on a 180-mesh sieve corresponded to a normal Portland Cement, so that the $2SiO_2.3H_2O$ or the γ-form is only present in the finer portion of the cement. Dyckerhoff [14] (who maintains that the β-form is the chief constituent of cement) has found that in the presence of free lime or of iron oxide, the γ-form is not produced.

The α- and β-dicalcium silicate set more slowly than normal Portland cement, but after a month's storage the paste is as hard and strong as that made with Portland cement. If, as has been suggested, that in normal cement lime is in solution or in colloidal suspension in the dicalcium silicate, the lime-water formed may increase the rate of setting and hardening of the silicate so as to equal that of Portland cement.

Dicalcium silicate is also readily hydrated by water in the presence of a solution of calcium aluminate and, according to Rankin, silica is released in the colloidal form. The hydration product, according to Klein and Phillips, forms a very granular porous mass with many voids, and is consequently less resistant to the freezing out of the salts from solution.

According to Rankin and Wright,[40] dicalcium silicate reacts very slowly with water and requires many months to develop strength. When it is wetted, the grains become covered with a coating of amorphous calcium hydrate which can be gradually leached out until only amorphous silica remains. Any crystals present are $Ca(OH)_2$. The rate of hydration increases with the temperature, which is raised when free lime or $3CaO.Al_2O_3$ is present.

Monocalcium silicate, $CaO.SiO_2$—the *meta*silicate—appears to have no hydraulic properties.

Hydrosilicates.—Klasse and Kühl [47] attempted to produce calcium hydrosilicates by double decomposition between aqueous solutions of definite sodium silicates and pure calcium nitrate. They found that sodium metasilicate produced $Ca.SiO_3nH_2O$ and sodium orthosilicate produced a precipitate in which the lime: silica ratio exceeded 1·5. In the presence of lime-water this rose to 1·76, from which it is inferred that calcium orthosilicate has a dimolecular structure, $Ca_4Si_2O_8$, and in the presence of water hydrolyzes to $Ca(OH)_2 + Ca_3Si_2O_6(OH)_2$.

Klasse considers that calcium hydrosilicates containing less lime than the metasilicate do not exist. Kühl concludes that Michaelis' view that "calcium hydrosilicates with a lime: silicate content higher than 3:2 do not exist" is untenable, and that if those with a lime: silica ratio of 2:1 only exist in the presence of free lime in solution the whole aspect of the amount of free lime produced by wetting cement is changed!

Free *silicic acid* seems scarcely likely to be present in wetted cements, as it would probably combine with any free lime also present. Yet Rankin has suggested that it is liberated in the colloidal state when tricalcium silicate is wetted. Such free silicic acid would form a gel with lime-water and so might be a valuable cementing agent.

Lime, when hydrated, first forms an amorphous material which later crys-

tallizes, though, according to Klein and Phillips [39] only the coarse grains of hard-burned lime form a crystalline product, the fine particles of low-burned lime forming an amorphous hydrate.

A. Zellweger [48] states that the first step in the slaking of lime consists in a colloidal swelling and the various other phenomena which accompany slaking are also due to colloidal action. He found a similar action occurs when magnesia is slaked.

Ray and Mathers [49] have found that slaked or hydrated lime exhibits various colloidal properties; the amount of colloidal lime present can be ascertained by cataphoresis. They found that a wet putty made by direct slaking differs from that made by wetting hydrated lime from the same source. The differences may be due to variations in the colloidal nature of the material, e.g. if the hydrate becomes too hot the gel is made irreversible. Most putties made from plastic lime have a higher colloidal content than those from non-plastic limes. In a plastic, slow-setting putty obtained by slaking with an excess of water, the particles have a positive electric charge.

The plasticity of a lime putty appears to be due to its retaining a film of water around each particle by a force depending on the electrical charge on each and differing with different limes.

Most hydrated limes require soaking for some time before they become plastic; some never become plastic. In the presence of free alumina or free silica, lime will enter into combination, forming a solution, a colloidal sol or gel or a mass of crystals, according to the conditions.

Alumino-silicates.—The hypothesis that Portland cement is a definite chemical compound of lime, alumina and silica and that its setting and hardening are due solely to the hydrolysis of this compound is simple and attractive, but, unfortunately, it is lacking in direct proof. W. and D. Asch, Feichtinger and others have also found experimentally that substances which can add hydroxyl (OH) groups at a definite rate to their molecule are hydraulites. The addition of water must be progressive and must not occur too rapidly. The experimental evidence suggests that any substance in which the addition of the OH-groups occurs slowly at first and progresses at a suitable rate until, finally, a very large number of OH-groups have been added, will form a harder and denser cement than if a smaller quantity of water had entered into the reaction or if the reaction had occurred more rapidly.*

The alumino-silicate which is best known in connection with cement is *jäneckite,* $8CaO.Al_2O_3.2SiO_2$. When wetted, it behaves very much like normal Portland cement. Unfortunately, its occurrence in such cement is problematical (*vide supra.*).

The extent to which other alumino-silicates exist in Portland and analogous cements is unknown.

Impurities.—The effect of iron compounds, calcined clay which has not combined with any lime, free quartz and various other minerals on the setting and hardening of cements has not been fully investigated. It is known that they enable a good clinker to be produced at a lower temperature than is needed for pure materials, but their precise action is largely unknown.

Iron compounds are commonly regarded as consisting mainly of ferric oxide, Fe_2O_3, but in most cements the iron is in the form of a silicate such as fayalite, $FeO.SiO_2$. Hansen and Bogue [50] found that in the system lime-silica-ferric oxide there are no ternary compounds and no mixed crystals. The

* The hardening of trasses and pozzuolanas with lime and water may be explained in an analogous manner. These "calcined clays" first react with lime and then add hydroxyl groups to the calcium salt first formed.

molten materials crystallize so rapidly as to make investigation very difficult. When alumina is also present, mixed crystals of ferrites and aluminates are produced.[51]

Investigations by Sosman and Merwin [52] on the system lime-ferric oxide and by Hansen, Brownmiller and Bogue [52] on the system, lime-alumina, ferric oxide show the existence of a definite dicalcium ferrite, $2CaO.Fe_2O_3$ and a monocalcium ferrite, $CaO.Fe_2O_3$, at almost all temperatures below 1,450° C. The monocalcium ferrite appears to form first and the dicalcium ferrite later, if sufficient lime is available. In mixtures containing more than 35 molecular per cent of ferric oxide, both the ferrites may be present so long as the temperature does not exceed 1,225° C.; above this temperature the monocalcium ferrite alone occurs unless there is a large excess of free lime. . Any dicalcium ferrite in cement is dissociated at 1,270° C. and if the clinker is heated to this temperature, or above, during manufacture the ferrite liberates red ferric oxide which imparts a red color to the quickly quenched clinker. If the clinker is cooled slowly, the ferric oxide and lime recombine and the red color disappears.

The dark color of cement clinker is largely due to the reducing atmosphere in the kiln, forming ferrous compounds which, in turn, form dark-colored silicates, principally fayalite, $FeO.SiO_2$.

It is curious that the inversion of β-$2CaO.Al_2O_3$ into the γ-form is not affected by the presence of iron oxide though a very small proportion of alumina is sufficient to stop it. Endell [53] has found that mixtures of lime, silica and iron oxides are devoid of hydraulic properties but Kühl [54] has produced good cements with a large iron content. Apparently a small proportion of alumina suffices to ensure hydraulicity. In most Portland cements the iron exists in the state of ferrous silicates which are dark-colored, but inert. Being more fusible than the essential constituents of the cement they remain in the glassy portions of the clinker (*belite* and *felite*).

Magnesia [55] in cements appears to be harmless if less than 8 per cent is present. When present, it is usually in the form of monticellite and spinel, and not as free magnesia as is sometimes stated.

Clay, at the temperature attained in burning cement is almost wholly converted into calcium silicates and aluminates. Any uncombined clay would probably be in the form of mullite, $(3Al_2O_3.2SiO_2)$, which is inert.

Quartz, including *sand,* is inert.

Alkalis—a term applied to soda and potash—are chiefly present as silicates and aluminates with no hydraulic properties and so are inert.

THE MECHANISM OF SETTING AND HARDENING

As will be realized, a separate consideration of each of the possible constituents of a Portland or analogous cement does not give a clear idea of the mechanism of setting and hardening.

The view is widely held that some of the foregoing substances occur in solution in each other in cement, so that their behavior as separate substances will not correspond to what actually occurs when a cement is mixed with water. The hydrolyzed products react with each other to a considerable extent though it is difficult to predict or measure it. The subject is still further complicated by the fact that commercial cements are made from impure materials which lower the temperature at which the clinker fuses, and facilitate several reactions which would not occur with pure materials.

Investigations made with commercial cements have led to two wholly different theories as to what occurs during setting and hardening; these are

sometimes referred to as the "crystal" theory and the "colloid" theory respectively, but it is important to remember that each theory is capable of many modifications and such a classification is more convenient than accurate. The true explanation of what occurs is probably to be found in a hypothesis which combines both the "crystal" and the "colloid" theories, by suggesting that the first products of the action of water on the cement are colloidal and that they gradually crystallize to an extent which depends upon the conditions under which the mixture is stored.

From the results just mentioned, it appears that the initial set of cements is due to the hydration of tricalcium aluminate, whilst the final hardening is due to the hydration of the tri- and disilicates of calcium. In the setting, both definitely crystalline and apparently colloidal material is produced. The problem is to find which material is the principal cause of the setting.

Crystal Theory.—The crystal theory was first elaborated by Le Chatelier,[15] who stated that "the anhydrous compounds in cements, not being in chemical equilibrium, immediately they come into contact with water are more soluble after hydration. For this reason, they form supersaturated solutions from which the hydrated compound crystallizes. The liquid, being then unsaturated, can re-dissolve more of the anhydrous material so that eventually, the whole mass crystallizes progressively. The entanglement of the needle-like crystals with each other is the only cause of the solidity of the mass; the finer and longer the crystals and the more numerous the points of contact, the greater will be the frictional resistance they offer to movement, and, therefore, the greater the strength of the mass." Le Chatelier considers that the "initial set" of cement is due to the reaction between water and calcium aluminate as follows:

$$3CaO.Al_2O_3 + 12H_2O = 3CaO.Al_2O_3.12H_2O,$$

and that the final setting of cement is due to the reaction between water and tricalcium silicate as follows:

$$3CaO.SiO_2 + 4.5H_2O = CaO.SiO_2.5H_2O + 2(CaO.H_2O).$$

No crystals of tricalcium silicate hydrate are ever seen—possibly because they are too small—but Le Chatelier argues from analogy that they are crystalline because crystals of hydrated lime and barium silicate are readily visible, and it is only reasonable to expect the calcium silicate to be crystalline; but as it is less soluble than the barium silicate, the crystals may be more minute. It is possible that, at first, the crystals may be colloidal, though this, according to Le Chatelier has nothing to do with the hardening of the cement.

H. Le Chatelier [56] has always regarded the colloid theory as "devoid of sense" because "substances are only exhibit colloidal phenomena in the presence of liquids in which they are insoluble," which is not the case with cement and water. He considers that although no crystals are visible at first, this is merely because they are too minute to be seen, but they grow rapidly under favorable conditions, as when a little of the apparently amorphous material is placed in a relatively large volume of water.

Various attempts to modify the rate of setting by the addition of "chemicals" to the cement have shown that sugar delays or prevents crystallization, even when only 3 per cent is present and causes the formation of an abnormal amount of gel matter which is responsible for the marked swelling and shrinkage and the softness of the products.[57] Several organic substances have a similar effect. In all cases where the crystallization is retarded, the strength of the mass is reduced. Sodium carbonate has the reverse effect of increasing

the amount of crystalline matter and accelerating the setting.[57] This seems to confirm the "crystal" theory. On the other hand, Shelton [58] has found that when a suspension of hydrated cement is treated with a solution of sodium or magnesium sulfate, the crystals disappear, leaving amorphous masses of gel which subsequently become granular.

It is highly probable that some of the crystals observed when wetted cement is examined under a microscope, are due to the experimental conditions. It is well known that an excess of water spoils cement and that the proportion of water used in hydrating cement is very important. Klein [59] has confirmed the results of Muth [60] which show that the more nearly the amount of water used on a microscope slide approximates to that used in actual practice, the less is the amount of crystallization observable in the early stages of setting and hardening. Muth [60] used 50, 100, 200, 500, 1,000 and even 4,000 cc. of water to 20 grams of cement and found that, in each case, needles formed most abundantly in the mixtures containing the most water, but if only a little water was present, the amount of colloidal matter was greatest and was at its maximum in the proportions of cement and water equally employed, as is common practice.

By substituting glycerin for the greater part of the water ordinarily used in examining cement under the microscope, Pulfrich and Linck [61] were able to limit the amount of water used to that required by the cement and yet to obtain microscopic slides in which the particles were sufficiently separated for observation. They found that glycerin has no action on the cement and the mixture richest in glycerin which had any effect on the cement contained 56 per cent by volume, of water. With a mixture containing 60 per cent of water, a gel was formed after 2 weeks, but no crystals. With 70 per cent of water, a gel was formed after 10 days, and united a fibrous mass of minute needles of calcium silicate. With 75 per cent of water, the needles increase chiefly in those parts where there is little cement-powder, whilst the gel forms where there is more cement. With larger proportions of water, the results resemble those obtained by previous investigators with plain water. Plates of calcium aluminate were not produced in glycerin mixtures containing less than 90 per cent of water. The authors conclude that contrary to others (who regard the setting of cement as due to the formation of a felted mass of crystalline needles) such needles only form where there is a very large excess of water (about 300 times the volume of the cement) and that with the proportions of water ordinarily used in making a cement paste (about 26 per cent) only gels are formed and that these are the cause of the setting and hardening of cement. The quantity of water usually mixed with cement is not sufficient to produce either silica needles, plates of calcium aluminate or any other crystals. The apparent conversion of crystals into gel on prolonged standing is not a simple change, but is due to the decomposition of the crystals as the inversion gel-crystal is not reversible. Pulfrich and Linck also conclude that calcium aluminate has no influence on the setting and hardening of the cement, but is useful in facilitating the formation of the clinker both in reducing the melting point and in increasing the "glassiness" of the clinker.

Thus, with an excess of water, crystallization may occur and lead to the theory suggested by Le Chatelier, but in the commercial uses of cement with a much smaller proportion of water, the silicates are only very slowly hydrated and the products appear to be calcium hydroxide and colloidal silicates, and possibly also colloidal silica.

The reaction may be analogous to that observed by Ostwald,[62] who has shown that barium sulfate when in very low or very high concentrations sepa-

rates out as a colloid, but with intermediate concentrations crystals are produced.* Bates [42] has also shown that calcium hydrate is only crystallized from calcium disilicate if the proportion of water is carefully controlled.

Another explanation of the crystallization may be that it is analogous to the results obtained by W. Doehle,[63] who found that the mercury salts of sulfuric acid formed gels with concentrations as low as 1 : 300. The gel gradually breaks up and the salt crystallizes out, the process being irreversible. Similarly in the case of camphoryl phenyl thiosemicarbazide [64] which, if dissolved in boiling alcohol and slowly cooled, produces large crystals; whereas, if cooled suddenly, a gel similar to silicic acid is produced, but being unstable it soon exudes liquid and at the same time crystallizes out.

Colloid Theory

The colloid theory of the setting and hardening of cements was originally proposed by W. Michaelis.[15] According to him, the first effect of the action of water on cement is the hydrolysis of the calcium aluminates present in the material. Two reactions are presumed to occur:

(1) On account of the presence of calcium sulfate a readily soluble compound $3CaO.Al_2O_3.3CaOSO_4.xH_2O$ is produced. This is dissolved and recrystallized in the form of needle-shaped crystals. The remainder of the aluminates is hydrated and dissolved less readily forming, on recrystallization, hexagonal plates.

(2) The second stage in the hydration consists in the hydrolysis of the silicates present. Michaelis suggested that the products formed are crystalline calcium hydroxide and colloidal hydrated calcium silicate. He stated that the latter material is invariably in the gel state, and that if the solution is sufficiently supersaturated, the aluminate may also occur in this form. He regarded hardening as due to the replacement of colloids by crystalloidal solutions and considers that the supersaturated solution from which needle crystals separate as having nothing to do with the hardening. Instead, the effective cause is now regarded as the formation of a hydrogel which unites the cement grains and contains calcium hydrosilicate and calcium aluminate. Through adsorption, more lime is absorbed and a typical opaque gel is produced. Michaelis also suggested that the outer layers of gel were further hardened by the adsorption of lime from the solution, so that the surface became more and more impermeable.

Shimizu [20] has shown that the changes in the electrical conductivity of a super-cement correspond to Michaelis' theory that the setting and hardening are colloid-chemical reactions. The initial rise in the conductivity curve corresponds to the formation of a *sol*, the next change corresponds to flocculation, new solid matter being separated from solution, the third change (accompanied by a rapid decrease in conductivity and rapid evolution of heat) indicates the formation of colloidal hydrated calcium alumino-silicate or silicate. The fourth and last change is attributed to a gradual increase in hardness during which the gel forms a coating around the cement particles, preventing further access of water to them, except by diffusion; and then the reaction continues slowly, more and more of the alumino-silicate or silicate being hydrolyzed and the lime set free adsorbed by the gel which brings about the hardening of the mass.

G. Becker [65] modified the theory of Michaelis by suggesting that the gelatinous membranes become stretched by osmotic pressure, and then, through adsorption, undergo a change similar to that involved in the lignification of

* P. P. von Weimarn was the first to bring this out. See his paper in Vol. I of this series. J. A.

plant fibers. He also gives rather more prominence to the effect of the crystalline products of hydration.

Under the microscope, K. Biehl [66] observed that when water was used to moisten the cement grains four distinct processes were observed:

(1) The formation of minute needle-like crystals;
(2) The formation of small plate-like crystals;
(3) The formation of a gel;
(4) The transformation of the gel into a crystalline mass.

Under normal conditions there is first seen to form about every cement particle, a gel of dicalcium silicate, the volume of which increases steadily until it fills all the interstices between the crystalline needles and also between the individual particles. The formation of this gel is, according to Wo. Ostwald,[62] the most important factor which gives to cement its specific hydraulic properties. The gel binds together the individual crystals surrounding a given cement particle and also the neighboring particles. The cement particles with their crystals become embedded in a common sheath of gelatinous substance and it is to this that the cement is presumed to use its solidity. Ambronn [67] described the swelling of the gelatinous sheath which forms around the particles and it has been photographed by G. Stein.[68]

When the gelatinous coating is formed on the surface of the grains of clinker, water is withdrawn from it by the unhydrated portion in the interior of the grains, so that the surface becomes hardened, whilst the interior is progressively hydrated, although, even after many years, the hydration is not complete.

The microscopical examination of cement mixed with a relatively large volume of water has shown that very fine needles of calcium silicate form first, then hexagonal tablets of a calcium aluminate and finally gelatinous drops which cause the needles to decompose in the gel. Finally hexagonal tablets of $Ca(OH_2)$ separate. Pulfrich and Linck [61] point out that if only 26 per cent of water is added, gels are formed, but crystals are only formed with an abundance of water. They regard hardening as due to the absorption of water which is facilitated by the growing gel. For this development, they say, a glassy material is best; crystallization is harmful in the clinker. Stern,[69] also, has drawn attention to the formation of microscopical colloidal layers around the cement grains and subsequent crystallization.

Rankin [40] attributes the setting and hardening to the formation of an amorphous material which, later, crystallizes. He has stated that "the initial setting is probably due to the hydration of $3CaO.Al_2O_3$; the early hardness to the cementing action of the amorphous material from this and $3CaO.SiO_2$. The gradual increase in strength is due to the further hydration of these two compounds, together with that of $2CaO.SiO_2$." Rankin regards the $3CaO.SiO_2$ as the best constituent in the cement; he considers that $2CaO.SiO_2$ requires too long to set and harden whilst $3CaO.Al_2O_3$ is too soluble in water.

Keisermann [70] studied the hardening of cements by means of dyes. He found that Patent Blue stains strongly alkaline sols of alumina and of aluminous substances, but does not stain silica or lime; that methylene blue in neutral or acid solutions stains free silica, but not silicates, and that anthrapurpurin in alcoholic solution stains all calcareous substances. When samples so stained were examined under the microscope under a magnification of 320 diameters, it was found that short, thick needles rapidly formed on the cement grains, these needles rapidly growing to small hexagonal plates. Later, small needles—very difficult to see—formed on the cement grains and formed a sort of halo around the latter. These small needles continued to form for several days, during

which time the plates grew considerably, showing their six sides more clearly each day. Finally, large hexagonal crystals appeared and enclosed everything else in the field of view, and at the same time, a gelatinous material was separated which retained its volume so long as water was present. When patent blue was introduced during the hydration, only the plates were stained, so that these plates must contain alumina in some form, whilst the gelatinous mass must be free from it. As alcoholic anthrapurpurin stained the whole of the preparations every substance in it must be calcareous; the hexagonal crystals and the gelatinous material appeared to be specially so. As methylene blue produced no stain, the hydrated cement appears to contain no free silica. If acetic acid is added to decompose the silicates, free silica is liberated and immediately stained. This was specially noticeable in the amorphous part of the product.

Blumenthal [71] considers that calcium metasilicates and aluminates are first formed as crystals, but that afterwards colloidal silicates are produced and consequently strengthen the mass by filling the pores and covering each crystal.

Against the colloid theory, Kanter [72] has shown that the formation of a gel does not occur with a very small proportion of water, but only with a far larger excess than can be used in practice and he regards unfavorably conclusions drawn from the use of so much water.

A further support of the view that the colloidal state of the hardened cement is only an intermediate one is given by Glasenapp,[73] who has shown that, in time, the gel crystallizes and that the crystalline state is the final one. Yet he has found that some cements contain colloidal matter for years, whilst others crystallize rapidly and completely.

Rohland has published numerous papers on the colloid theory of cement and has set out clearly the hydrolytic changes due to water and the colloidal changes due to the coagulation of lime alumino-silicates, silicic acid and aluminium hydroxide in the presence of hydroxyl ions which then act as a bond and also cause the shrinkage. According to Rohland, the colloidal products are not stoichiometric compounds, but variable aggregates. Kühl [74] regards the formation of colloids as the first stage and their gradual conversion into crystals as the real cause of hardening. Würzner [75] regards hardening as due to capillary action on crystallizible or gel-forming materials.

Beckmann [30] confirms Kühl, and regards hardening as due to a flocculation produced by electrolytes or highly concentrated sols, the dicalcium silicates being dissociated into lime and colloidal silica. The solution causes a drop in temperature and the resulting calcium ions cause a rise in the electrical conductivity. If the solution is sufficiently concentrated calcium hydrosilicate separates as a gel and absorbs $Ca^{\cdot\cdot}$-ions which reduce the electrical conductivity. He adds that the rapid coagulation of the tricalcium silicate is the chief phenomena from the start.

That crystals are unimportant is shown by the fact that the Röntgen-spectra of clinker and set cement are identical. Schneider [76] considers a zeolite residue $CaAl_2Si_4O_{12}$ to form and react with water in the presence of lime, separating $3CaO.Al_2O_3$ in a hydrated state.

Rosenhain [77] has argued in favor of the colloidal theory by assuming the solid grains to be initially surrounded by a solution of some constituent, which solidifies owing to the removal of water by percolation or chemical action. The resulting films or layers impart great hardness and strength to the whole mass.

Maeda [78] approaches the problem from another standpoint and having investigated magnesium chloride (Sorel) cements (*vide supra*), he concludes

that supersaturation and recrystallization are the chief factors in the setting and hardening of Portland cements, but the simultaneous occurrence of adsorption phenomena is also important, particularly what he terms "superficial hydration" which occurs on the surface of extremely small crystals, i.e., those of colloidal dimensions. Unlike other investigators, Maeda attaches little importance to large and easily recognized crystals, but regards sub-microscopic crystals as the chief factor in setting and hardening.

Catalytic Theory

A catalytic theory has been mentioned by several investigators who explain that the setting is started by a chemical substance (catalyst) present in very small proportions in the cement or water. No conclusive investigations have as yet been made, but some experiments by F. Tippmann [79] seem to indicate that the setting is started by dissociated SO_4-ions present in the clinker, as cements which are quite free from sulfate behave very differently from ordinary Portland cement and do not swell in water, even after a year, yet when mixed with a small proportion of gypsum, they swell to 200 to 300 times their original volume in 2 minutes. The addition of lime-water to sulfur-free cements has no effect, but free sulfuric acid acts like gypsum. In the absence of sulfate-ions, no colloidal gel is formed, but if the cement contains only 0.3 per cent of gypsum, abundant colloidal matter is produced on immersing the clinker in water. He found that, in addition to retarding the setting, gypsum inhibits the formation of crystals of calcium hydroxide. He attributes the expansion and cracking of some cement pats to an excess of gypsum which decomposes the colloidal gel liberated by a very small proportion of gypsum.

"Combined" Theory

The "combined" hypothesis is an attempt to reconcile the crystal and colloid theories. It is well represented by Baykoff, who suggests that setting occurs in three stages:

(1) *Solution* in which the liquid is progressively saturated with the different soluble substances.

(2) *Colloidization,* in which the products of chemical reactions are obtained in the colloidal state—this stage corresponding with the initial set.

(3) *Crystallization* in which the gels are transformed into aggregates of larger crystals.

The possibility that much of the colloidal matter, whilst apparently amorphous, may actually be in the form of crystals must not be overlooked, as P. Scherrer and Sir W. Bragg have shown that many colloidal substances are minutely crystalline. This is the more probable, as it is known that the passage of other colloidal substances into the crystalline form is a continuous similar process to the growth of crystals from a microcrystalline nucleus.

The "combined theory" is also held by (*a*) Gessner [80] who, "having studied the literature exhaustively," concludes that from the point of view of the colloid chemist a somewhat elaborated version of Michaelis' theory agrees best with the results, and by (*b*) Bogue,[81] who, after a similar study, has reached the conclusion that the two theories are not so seriously in opposition as is commonly supposed. The modern view may be expressed by saying that the present tendency is towards an acceptance of the general principle of crystallization as set forth by Le Chatelier, Donnan and others, but simultaneously to recognize the importance of the rôle played by the amorphous or colloidal material, as emphasized by Michaelis, Kühl and others. A detailed examina-

tion leads to the conclusion that the distinction between the two theories is more superficial than fundamental, as the same forces and phenomena are implied in both theories; the difference is largely due to the placing of the emphasis on either the crystalline or the amorphous material.

The following order of reactions which occur when a Portland or analogous cement is mixed with a suitable amount of water is as nearly correct as can, at present, be ascertained:

Setting

(1) Any tricalcium silicate or any solution of lime in β-dicalcium silicate is hydrolyzed and the liberated lime is hydrated, some being dissolved in the water. The hydrolysis of the tricalcium silicate is regarded by Rankin [40] and also by Klein and Phillips,[39] as being complete in seven days. Bates and Klein [43] regard the dicalcium silicate as hydrolyzing very slowly in water and more quickly in the presence of free lime, but state that after 28 days (or less) it produces as strong a mass as the tricalcium silicate. For this reason, they consider that an ideal cement should contain an excess of the dicalcium silicate to give strength at a later stage in the hardening.

(2) Any calcium aluminate present is hydrolyzed, and in the presence of free lime sets rapidly. Klein and Phillips [39] state that tricalcium aluminate begins to set before any other constituent, but if not present in excess it assists the hardening. The foregoing reactions are facilitated by the lime in solution, this being more reactive than plain water.

(3) Simultaneously with the hydrolysis and decomposition of the aluminates and silicates, some free hydrated (colloidal) alumina appears to be produced.

(4) If any calcium sulfate is present, it reacts with the cement, forming calcium sulfo-aluminate which quickly crystallizes.

(5) Any alumino-silicates, ferrates and ferro-silicates are hydrolyzed in a similar manner and form either colloidal products or add to the complexity of the interlocking silicate and aluminate crystals. Some iron appears to remain as an inert hydroxide. The first products of the reactions appear to be amorphous and colloidal, but in the presence of lime-water a considerable amount of crystalline matter is produced.

When the foregoing reactions are sufficiently advanced, the paste becomes rigid and is said to be set. There is no natural point which can be defined at the end of the setting, but for convenience it is regarded as being reached when a Vicat needle scarcely makes any impression. This is a wholly arbitrary point. The rate of setting depends on the fineness of the cement, the temperature at which it was burned (the free lime in underburned cement causing it to set slowly, as lime is a product of the hydrolysis), the proportion of calcium sulfate and of water present and the temperature of the materials.

Hardening

When the mass has set, the reactions continue, the dicalcium silicate and some of the minor constituents being hydrolyzed more slowly than the rest, so that the maximum strength is not gained for several days.

According to Klein and Phillips,[39] the early strength (during the first 24 hours) is probably due to the hydration of free lime and the aluminates. The later increase (between 24 hours and 7 days) depends on the hydration of the tricalcium silicate, though a further hydration of aluminates may contribute.

The increase between 7 and 28 days is attributed by Klein and Phillips to the hydration of β-$2CaO.SiO_2$, but here are encountered opposing forces, in the

hydration of any hard-burned free lime and in the crystallization of the aluminates. This hydration causes the drop in strength, after 7 days, of hard-burned cement, whereas the decrease shown by high alumina cements is due to the crystallization of the aluminate. Between 7 and 28 days, the aluminate crystallizes and β-$2CaO.SiO_2$ begins to hydrate. This is regarded by Klein and Phillips as the chief constituent of the American cements, but is the least reactive.

With a normal Portland cement, about a month is required to approach the maximum strength, but with a rapid-hardening cement, a week is sufficient; many cements continue to increase in strength for several years.

The rate of hardening depends on the fineness of the cement, the proportion of water used and the temperature at which the mixture is maintained.

It is very important to keep the cement sufficiently wet during the hardening period or the strength of the mass will not be fully developed, and an objectionable defect known as *dusting* may occur later.

Apparently no one theory will completely explain all the phenomena observable in the setting and hardening of cements. No exclusively chemical theory is able to explain the physical accompaniments which are so characteristic of the setting and hardening, and no physical theory alone will explain the chemical changes which occur.

Chemical reactions associated with hydration take place between many substances without developing the characteristic physical properties observed in mortars and cements. In the setting and hardening of these substances, there must, therefore, take place certain special changes, beside the chemical ones, which are responsible for the physical properties resulting from these reactions; it is these special changes which are regarded as being colloidal in character.

Colloidal Phenomena in Wetted Cements

When a Portland or similar cement is mixed with water, with or without the addition of sand, various colloidal phenomena may be observed of which the most important are:

(1) **Expansion and Contraction.** A well-known characteristic of "dry" colloidal gels is their property of swelling when immersed in water or in very dilute solutions of acids or alkalis and of shrinking when dried. This swelling occurs when cement is mixed with sufficient water to make a soft paste, though it is appreciable only when accurately measured. This is fortunate, as an appreciable swelling of the cement during the hardening is very objectionable, and cement manufacturers take special care to avoid producing cements with this property.

Some measurements made by Gessner [82] show that with a good Portland cement, the volume of cement and water in a mixture is less than the sum of their separate volumes, and diminishes rapidly during the first five days, then more slowly for 20 days, and still more slowly for 275 days, when the observations ceased. The decrease in volume is 3 per cent up to 24 hours and 6 to 9 per cent after 3 months. Hydraulic limes showed smaller decreases and aluminous cements greater decreases in volume than Portland cement. The swelling is much greater when Portland cement is immersed in lime-water [83] or when a cement containing an excess of free lime is heated in steam; in the latter case, the expansion may be so great that serious cracking occurs. The addition of clay to a cement, or the presence of clay in a sand added to cement, will produce a marked expansion.

The cement paste shrinks on drying, and in this way greatly resembles

other colloidal gels. The dehydrated material is hard and impervious. Its behavior is very similar to that of colloidal silica which is suggested by Rankin to be an important material in the hardening of cements. When colloidal silica is kept, it gradually becames gelatinous and begins to harden. In time, it forms a hard, horny and insoluble mass, like flint, which is an example of a hardened silica gel.

If the shrinkage on drying is sufficiently great, cracks will be formed; they occur more frequently in lean than in plastic mixtures.

If a bar made of neat cement and water is exposed to an atmosphere of varying humidity, the bar will expand as it absorbs moisture and will contract as it dries. The variation in length between the dry and saturated state is about 0.5 per cent. of the average length.[84] This change is attributed to colloidal matter in the mixture of cement and water. The extent of the expansion or contraction necessarily varies on the conditions of storage (*vide Ageing, infra*).

(2) **Plasticity.** The paste produced by mixing cement with water is (temporarily) plastic. According to Rohland[85] the plasticity of a freshly made mixture of cement and water is due to the formation of a colloidal gel—colloidal gel and plasticity being very closely related in many substances.[86] If an excess of water is added to the cement, its plasticity is destroyed and the strength of the hardened mass is greatly reduced. To avoid this unnecessary loss proper attention should be paid to the proportion of water added; this is commonly known as the water-ratio.

According to Abrams,[87] the optimum proportions of Portland cement and water are shown by the equation *:

$$\frac{W}{C} = x$$

where x is an exponent in the equation,

$$S = \frac{14{,}000}{7^x}$$

S being the compressive strength (in lb. per sq. in.) of the mixture of cement and water made into a cylinder 12 in. by 6 in. and stored for 28 days in a moist room at 70° F. before the strength is determined. The numerical constants in the equation depend on the cement and mode of testing but are usually assumed to be correct for all Portland cements.

In addition to the correct proportion of water, any sand or other aggregate added must be suitably graded and used in suitable amounts.

Bolomey[88] uses a different formula, viz.,

$$\left(\frac{c}{w} - 0.5\right)k.$$

The American Society for Testing Materials Committee has suggested that the water ratio should give a compressive strength of 1,000 to 4,000 lb. per sq. in. at 28 days; with normal Portland cements this corresponds to a ratio of 0·65 to 1·30.

It is not sufficient to add the same proportion of water to all Portland cements as the water-requirement of individual cements differs considerably and must be allowed for, as shown by the above equation.

* Abram's original equation is probably slightly low for the better cements, now available, but not too low for the ordinary ones.

The advantages of adding the water in the optimum proportion to the cement are: (1) a superior concrete is produced; (2) the consistency is more uniform; (3) more concrete can be placed in a given time, as placing is easier, and (4) a concrete of greater strength is obtained or a smaller proportion of cement is needed to attain normal strength.

In comparing various reports of investigations on the water-ratio, it is important to remember that, owing to small differences in the methods of testing and in units of measurement, some American and English data on water-ratios do not correspond closely.

(3) **Viscosity.** A properly made cement-paste prior to setting is highly viscous. According to Gessner,[82] the viscosity increases slowly and is more marked after 1½ hours, indicating the formation of a gel. A study of the viscosity of such pastes is peculiarly difficult, as unless special care is taken the gel structure is destroyed without its destruction being recognized.

The fact that, in the manufacture of asbestos cement sheets, the mixture is allowed to stiffen slightly and is then subjected to great pressure, appears to support the colloidal theory, for, as Michaelis has shown, if the setting of the cement were due to crystallization alone, the disturbance of structure by the pressure applied to the crystals would reduce the strength of the material as a whole. If, on the contrary, the setting were a colloidal phenomenon, and the final hardening a conversion of the colloid into a crystalline product, the increase of strength, due to pressure, would be explained.

(4) **Structure.** There appears to be a large proportion of amorphous (gel-like) material in a wetted cement, at any rate in the early stages of hardening. Von Glasenapp[89] states that the ground mass in hardened cement consists of a colloidal gel, which retains its colloidal character even after one year, the opacity increasing with age. It is to this that he attributes the hardening of the cement. If the "structure" formed during the setting is disturbed, e.g., by unduly prolonged mixing or by delay in placing the material, the strength will be seriously reduced. This loss of strength after disturbance is characteristic of colloidal gels; it also occurs when a felted mass of minute crystals is disturbed.

(5) **Binding Power.** Portland cement possesses so high a binding power that it may be mixed with six or more times its volume of sand and yet the product will be plastic when mixed with water.

(6) **Mechanical Strength.** The increase in strength of cement in one day can be much more easily understood if it is considered to be due to the formation of a hard gel than to the formation of interlaced crystals. According to Klein and Phillips,[39] the crystallization of calcium hydrate and calcium aluminates causes a decrease in the strength of cements. This is often observed in cements with a high lime or high alumina content between 7 and 28 days; it may be due to the expansion of the material on crystallizing and to the consequent setting up of stresses in the material. The toughness and cohesion of the cement paste are indicative of a colloidal gel. The strength produced by coagulated colloids is quite different from that produced by interlocked crystals, that of glue being a typical example of the great strength of coagulated colloids. In this respect, cements would appear to be much more dependent for their strength on colloidal phenomena than on the interlacing of needle-shaped crystals. This is not conclusive, however, as some of the strongest materials, e.g., metals and rocks, are largely crystalline.*

* Larger crystals tend to break along cleavage planes and are relatively weak, while with colloids the enormous surface and lack of long cleavage planes make for strength. With metals and minerals the finer the crystals, the harder or stronger the mass, *up to the zone of maximum colloidality*, after which, as the dispersion verges toward true solution, the tendency is toward softening. Thus ballas and carbons are harder even than diamond. J. A.

In favor of the view that the strength of cement is due to the colloidal material present is Hedström and Werner's [90] discovery that the tensile strength varies as the square of the quantity of cement hydrated in a given time and can be calculated from a knowledge of the distribution of the particles and of their sizes. The rate of hydration depends on the total surface area of the cement particles. These investigators also found that the tensile strength varies inversely as the square of the water: cement ratio and that comparatively slight differences in the size of the particles cause great changes in the time required to attain any definite tensile strength. This is a further indication of colloidal reactions as distinct from solution and recrystallization.

Kühl [91] has shown that the maximum strength is not developed with the smallest particles of cement. It is not the "fineness" but the most effective size of particle which is important and when that size has been reached further grinding does harm. If colloidal clay is added to a cement a marked reduction occurs in the strength; this corresponds to the known result of mixing two colloidal gels.

(7) **Adhesion.** Rohland claims that no non-colloidal or crystalline substance has the tenacity of cement for steel reinforcement, and, therefore, concludes that their mutual adhesion must be due to the colloidal nature of the cement. Unfortunately, it is almost impossible to ascertain accurately the causes of such adhesion. It is a resultant of several forces, but the origin of those is not known with certainty.

(8) **Heat of Hydration.** The rise in temperature found when cement sets is characteristic of the setting of colloidal substances. Thus, Zsigmondy [92] found that the setting of a 5 per cent jelly of silicic acid produced a rise in temperature of 1·1° C., which is equivalent to about 20 calories per gram, a figure which is similar to that obtained when cement hardens, if no correction is made for radiation losses in either case.

The great evolution of heat is attributed by Beckmann [93] to the so-called tricalcium silicate, $3CaO.SiO_2$, not being a single chemical compound, but a dicalcium silicate with lime in solid solution; the development of heat is attributed first to the free lime slaking in the water and later to the hydration of the disilicate. Beckmann also found that α- and β-$2CaO.SiO_2$ gave first a fall and then a rise in temperature; the γ modification did not show this. This confirms Dyckerhoff's views (*vide supra*). According to Killig [94] the first rise in temperature corresponds to the formation of tricalcium aluminate and the subsequent rise to the crystallization of monocalcium silicate. The latter phase has been confirmed by Kerserman, Blumenthal and others. Aluminous cements when mixed with water, develop much more heat than Portland cements.

(9) **Effect of Temperature.** The time required for setting is increased when the temperature of the mixture of cement and water is lowered. Several attempts [95] have been made to find a formula correlating the rate of setting and the temperature, but with no really satisfactory result. Different brands of rapid-hardening Portland cements have very different setting times and the effect of lowering the temperature differs with each cement. It is easy so to increase the time required for a rapid-hardening cement by working at a low temperature that such cement has no advantage over an ordinary Portland cement. Setting cannot occur if the temperature is so low that the water freezes because the reactions which take place during setting and hardening require liquid water to be present. If freezing is prevented by keeping the materials at a temperature just above 0° C. or if the freezing point of water is lowered by the addition of salt or other "anti-freezing" mixtures, the setting

and hardening will continue, but at a lower rate than if the materials are at a higher temperature. The use of anti-freezing materials is deprecated.

The effect of freezing is most serious between the "initial" and "final" setting. If a cement freezes solid before the "initial set" takes place, no serious damage results. The mass remains in a dormant state until the ice melts and turns once more into water. If, however, the gaging water freezes after the "initial set" has taken place and before the "final set," the expansion of the ice forces apart the young crystals, and entirely prevents their knitting together.* Once forced apart, they will never knit together again, and the mass is utterly ruined as it has no strength. Aluminous cements, on the contrary, develop so much heat during setting that they are not affected by frost.

Temperatures higher than normal increase the rate of setting but with more likelihood of inducing internal stresses. Thus, when a mixture of cement and water is kept in an atmosphere of saturated steam at 100° to 200° C. for 48 hours, the rate of hydration and the amount of gel formed are increased according to the temperature of the steam. Crystals of calcium hydroxide appear almost immediately on steaming, increase in amount as the temperature is maintained, but disappear almost completely after 48 hours.

Concurrently, a new crystalline product appears and increases as the lime is reduced, reaching a maximum at 150° C. The new crystals appear to be a calcium silicate containing very little silica and resistant to sulfate solutions.

The published data, though numerous, relate to so few tests on each material that it is impossible to generalize more than by saying that low temperatures tend to cause slow setting and higher temperatures quick setting. On aluminous cements, low temperatures have little effect on the setting, but may reduce the strength.

McDaniel [96] and others have found that by mixing and allowing to set at the normal temperature (60° F.) but subsequently storing or curing at 95° F. greater strengths were obtained.

Biehl [97] has found that test-pieces can attain in 8 hours the strength normally attained in 28 days if they are cured in steam at 16 atmospheres (200° C.) for 8 hours. Larger masses cannot be treated effectively. The difficulties experienced in maintaining large masses of concrete at a high temperature are so serious that hot-curing is seldom attempted, nor is it of great commercial value on account of the liability to develop internal strains. The exposure of wetted cement to *frost* should always be avoided until the material has become sufficiently hardened to withstand the frost. Aluminous cements are less liable to damage by a mild frost than are Portland cements, but a severe frost will damage any kind of freshly-placed cement (*vide "Curing," infra*).

(10) **Electrical Conductivity.** A hardened Portland cement is a semi-conductor but owing to polarization, measurements can only be carried out by Kohlrausch's method [98] using an alternating current. Shimizu [99] has found that when a mixture of Portland cement and water is kept at a constant temperature during setting and hardening the electrical resistance changes suddenly at a point in the conductivity-time graph which corresponds to the final set. He claims that this is a more accurate basis of measurement than the mechanical and thermal methods generally used.

Beckmann [80] found that, with γ-2CaO.SiO$_2$, no change in conductivity but with the α- and β-forms a rise, and, after a peak, a fall in conductivity occurs. Synthetic 3CaO.SiO$_2$ shows a reduction in conductivity. Hence, according to Beckmann, there appear to be two opposing sets of reactions, one of which

* This is analogous to the evil effects of freezing on starch pastes and most glues, which results in a dehydration. J. A.

increases the electrical conductivity and the other diminishes it. It is possible that Beckmann's results are affected by polarization.[99]

In the electrical conductivity-time curve of aluminous cements, two breaks are observed, the first corresponding to the hydration of the calcium aluminate and the second to that of the calcium alumino-silicate or silicate. In rapid-hardening Portland cements only one break occurs corresponding to the hydration of the calcium alumino-silicate or silicate. As, in Portland cements, there is no break corresponding to monocalcium aluminate, Shimizu[89] concludes that this substance does not occur in such cements.

The few investigations made on the *cataphoresis* of Portland cement paste are at present inconclusive, but the destructive effect of electric currents on damp concrete are sufficiently analogous to the well-known cataphoretic phenomena usually associated with colloids to make further investigations attractive.

Electrolytes—even in the small proportions in which they occur as impurities—have an important effect on the setting of colloids. Thus, colloidal silicic acid may be coagulated in a few minutes by the presence of a 0·0001 per cent solution of an alkaline or earthy carbonate, whilst colloidal alumina is readily coagulated by very minute proportions of potassium sulfate, etc. It is very probable that the variations in hardening power of different samples of Portland cement is dependent far more on the presence of minute proportion of impurities than is commonly realized, as unless some action of this kind does occur, some of the variations are inexplicable. The effect of electrolytes, however, is by no means properly understood at present; many of them are very irregular in their action, so that there is great difficulty in drawing correct conclusions from results of experiments. Some investigators have suggested that electrolytes act as coagulants or deflocculants, whilst others prefer to regard their action as due to their affinity for water, those substances which abstract water from the hydrated film on the cement particles increasing the rate of setting, whilst salts containing water of crystallization add to the amount of water in the film and retard the setting.

(11) **Adsorption.** The selective power of adsorbing certain dyes and removing them from solution is a typical characteristic of colloidal gels. Cement has been found by Keisermann[100] to exhibit this phenomenon. Rohland[101] and Stern[102] have also shown that the apparently colloidal constituents in cement can be dyed by immersion in a solution of eosin or some other dye. Desch and Le Chatelier have independently attempted to reproduce Keisermann's results, but have not been successful, probably on account of the different conditions under which they worked. Ostwald found that the apparently colloidal material could readily be stained by dyes such as anthrapurpurin. F. Blumenthal[103] from investigations with dyes, has stated that the setting of cement is due solely to the crystallization of monocalcium silicate and the later hardening to the binding of the crystals by means of a gelatinous silicate.

(12) **Ca-ion Concentration.** Beckmann[80] has investigated the Ca-ion concentration in various substances when mixed with water. With tricalcium silicate a strongly marked maximum is reached and is attributed to the coagulation of hydrosilicates and the liberation of large quantities of lime or alternatively to the tricalcium silicate being a solution of lime in dicalcium silicate, both of which are hydrolyzed by the water and all the free lime entering into solution.

(13) **Aging and Storage.** The changes which take place when cement is stored are analogous to those undergone by other colloids. P. H. Bates[104] found that concretes made using calcium aluminates as cement were reduced

in strength when stored in water or in a damp place on account of the cement being colloidal and absorbing moisture in the consequent swelling. A. H. White [105] has stated that concrete can retain colloidal properties to an undiminished extent for at least twenty years. He has also found that the extent of the changes in volume undergone by cement depends on the conditions of storage during the early stages. Any free lime present causes undue expansion during the first few weeks but not after one year. Magnesium silicate is harmless but free magnesia causes slight additional expansion for several years. Magnesia causes no trouble in concrete kept continuously in air. A larger proportion of iron oxide decreases the changes in volume: alumina has the opposite effect. Prolonged storage has no effect on the normal changes in volume due to variations in temperature.

According to Abrams,[106] the storage of cement in bins shows little deterioration in five years. The loss of strength of Portland cement when stored in bags for five years is no greater than that after two years. Storage has little effect on fineness, soundness, consistence, and setting-time but may reduce the time of setting if the storage is very prolonged. Cements with the greatest moisture and carbon dioxide contents show the most deterioration on storage.

The expansion of bars of cement when placed in water and their contraction on removal and storage in air are typically colloidal phenomena. It was found [107] that when a bar of cement was taken out of water it contracted gradually for 60 days. On re-immersing, there was a considerable expansion for the first week and much less in further weeks, the total elongation being 0·15 per cent.

(14) **Specific Gravity.** The true specific gravity of hardened cement is much lower than that of the crystals of the various silicates and aluminates presumed to be present in the clinker. The evidence shown by specific gravity is not very clear, however, as the reduction may be due to the formation of a colloid or of a crystalline hydrate.

(15) **Impermeability.** The impermeability of cement to water is more characteristic of a colloidal material than of a felted mass of crystals, unless the interstices between the crystals were filled with a colloidal or other amorphous material.

Varying the Rate of Setting

It is very important that the rate at which a cement sets should be suitable for the purpose for which the cement is used. Otherwise, the material may have begun to set before it has been properly placed in position or, alternatively, the setting may be so slow as to be very inconvenient.

The setting can be *accelerated* (i.e., the time required can be reduced) by the addition of caustic soda, sodium carbonate, common salt or the corresponding potassium compounds, magnesium chloride, aluminum chloride, aluminium sulphate, alum and potassium sulphide.

The setting can be *retarded* (i.e., the time required may be increased) by (1) using insufficiently burned clinker; (2) using cement which has been exposed to the air (i.e., aerated), or (3) adding a small proportion of a retarding agent, some form of calcium sulfate being usually employed. Other salts, such as potassium dichromate, boric acid, borax, sodium sulfate, and potassium sulfate may be used. Various other salts produce a retardation when used in small quantities and an acceleration when larger proportions are used, though the results of investigations on this subject are far from conclusive and are, in some instances, mutually incompatible.

The effect of a catalyst on the setting and hardening of cements has not

been properly investigated. It ought to be possible to increase the speed of either setting or hardening by this means, but though White [108] has tried several substances no satisfactory one for accelerating the hardening has been found.

The precise action of accelerators and retarders of the setting is not clear. Meade [109] concludes that the *index of activity* (i.e., the silica: alumina ratio) is the most potent factor in controlling setting time, ratios lower than 2·3 usually produce rapid setting cements and those above 5·0 slow setting cements.

Aeration or exposure of cement to the atmosphere reduces the rate of setting and so acts as a retarder. It also hydrates any finely divided particles of free lime which may be present, and so reduces their tendency to expand or "blow" at a later stage in the use of the cement. The changes which occur in aeration are similar to those effected by water, but the small proportion of water present in the atmosphere makes the changes much slower. The carbon dioxide in the air converts any hydrated lime into microscopic crystals of calcium carbonate and so renders them inert. Excessive exposure to air reduces the value of the cement by effecting the hydrolysis and carbonation of the finest and, therefore, most valuable particles.

The earlier cements were improved by aeration, which hydrated any quicklime present and so reduced it to a fine powder, but well-made modern cements are *not* improved by this treatment. Nevertheless, it is a wise precaution, when testing cements which yield unsatisfactory results, to expose them to the air for three or four days and then test again; they will then, in many cases, yield satisfactory results.

Exposure to air is really equivalent to exposure to moisture, and steam is, therefore, used as a retarding agent with good effect. The retardation effected by water or steam is due to the hydration of a small portion of the cement and the consequent liberation of a little free calcium hydrate. When the clinker is treated with steam so that about 1 per cent of water is absorbed, the proportion of calcium sulfate required is reduced to about one-half that otherwise needed.

Retarders. By far the most popular retarder is some form of calcium sulfate, gypsum, plaster of Paris and anhydrite or a mixture of gypsum and anhydrite being generally used. The relative values of gypsum and anhydrite have not been definitely established. Meade has found that (1) gypsum is an effective and safe retarder; (2) the SO_3 in anhydrite is as effective as the same amount of SO_3 in gypsum; (3) mixtures are effective in proportion to the amount of SO_3 present; (4) anhydrite is a good retarder and is neither injurious nor inert. Killig [111] disagrees and finds that four parts of anhydrite are needed to effect the same retardation as one part of gypsum. Dahlgren [112] found that a gypsum containing 51·25 per cent of anhydrite failed as a retarder. Platzman [113] and Berger [114] found independently—that the retarding action of gypsum anhydrite and plaster of Paris is proportional to their solubility.

Berger [114] finds no marked difference in the action of the various forms of anhydrite but the fineness of the anhydrite is of great importance. Cement retarded by gypsum is more plastic than that retarded with anhydrite. He agrees with Killig that when anhydrite is used a higher percentage of SO_3 is required than for a cement retarded with gypsum or plaster of Paris and finds it impossible to retard with anhydrite a clinker which requires the maximum amount of gypsum. He also found that the strength of cement retarded with plaster of Paris is generally higher than of that retarded with anhydrite or gypsum alone, but cement containing an equivalent mixture of anhydrite and plaster of Paris is as strong as cement containing any other form of calcium sulfate. Better and more uniform results were obtained

by grinding the retarder with the clinker than could be obtained by grinding each separately, and then mixing without further grinding.

A study of the pH value of the cement solution shows that there is a direct relation between the alkalinity and the SO_3 content of the solution. Whether the pH is the controlling or only an accompanying factor in the setting has not been determined.

Budnikov [115] has found that, if a suitable catalyst is present, anhydrite reacts rapidly with water, due to the formation of unstable, complex hydrates which readily decompose, forming gypsum ($CaSO_4.2H_2O$). Kühl [116] has suggested that when gypsum is ground with warm cement-clinker, it is converted into plaster of Paris, unless the gypsum is overheated, when it is converted into anhydrite.

The precise nature of the action of calcium sulfate on cement is not fully understood. As the amount required is only 2 to 3 per cent of the weight of cement, its action may be largely catalytic. According to H. Kühl it "increases the concentration of the aluminous ions and so favors gelatinization" provided sufficient calcium sulfate is present to produce rapidly a saturated solution of this substance.

E. Candlot has stated that a double salt—known as "Candlot's salt" and corresponding to the formula $3CaO.Al_2O_3.3CaSO_4.3H_2O$—is formed by the interaction of calcium sulfate and cement, and that this compound is insoluble in water and so converts any aluminate into a form which takes no part in the setting. This explanation is widely accepted, but can hardly be said to meet the facts. Candlot endeavored to remove some of the objections to this theory by postulating that a certain quantity of free lime is necessary in order that the gypsum may have its effect. It is true that a partially hydrated cement is retarded by a much smaller quantity of calcium sulfate than a cement which has not been treated with steam or moisture, but this does not necessarily prove Candlot's theory. A more probable explanation is that the calcium sulfate dissolves at such a rate that its saturated solution prevents the hydrolysis of the cement by enabling only a very small proportion of lime to be liberated and dissolved at a time. Whichever theory be adopted, it is a curious fact that the highly soluble calcium chloride has an even stronger retarding action than calcium sulfate, but magnesium chloride (which is also readily soluble) accelerates the setting. This implies that it is the acid portion of the material (SO_4, Cl, etc.) which is the active agent, and that some combination of these ions and the cement molecule occurs. The destructive action of sulfate solutions, and particularly of sea-water on cement immersed in them, confirms the opinion that some reaction occurs between the SO_4-ion and the cement.

F. Tippmann [76] has pointed out that the effect of an increasing content of gypsum on the setting and hardening times of a cement is very striking; the setting time remains almost constant, but the time of hardening increases with the proportion of gypsum, i.e., with the proportion of colloidal matter, up to a limit, beyond which the gypsum begins to have a destructive action. In short, a little gypsum restricts crystallization and facilitates the formation of a colloidal gel. F. Tippmann claims to have shown that a quick-setting cement owes this property to crystallization from a supersaturated solution and a slow-setting cement to the much slower coagulation of a supersaturated highly dispersed colloidal sol.

The retarding action of calcium sulfate is diminished by storing the cement. This has been explained as being due to the gradual carbonation of the lime set free by the sulfate and moisture, but it is equally probable that a combina-

tion between the sulfate and the cement occurs on long storage or on exposure to the atmosphere.

Calcium sulfate is usually added to cement clinker in the form of gypsum, the materials being ground together. Finely powdered gypsum may also be added to the ground cement, but for this purpose it is preferable to use plaster of Paris, which is obtainable in a much finer state of powder than is gypsum. The difference has been explained by Kühl [116] who found that when gypsum is ground with the warm cement clinker, the temperature in the mill is sufficient to convert it into plaster of Paris ($2CaSO_4.H_2O$), but if the mill is too hot the plaster may become overheated and converted into anhydrite.

Experiments as to the effect of the addition of 2 to 3 per cent of calcium sulfate to various quick-setting cements show curiously irregular results, and indicate that the action of this substance is by no means so simple as is sometimes supposed. Some of the discrepancies may be due to lack of uniformity in the cement itself or to irregular admixture of the retarding agent. Whatever the cause, the disadvantages of adding a retarder to some cements should not be overlooked, and the amount used should be kept as small as possible.

The whole subject of the action of retarding agents and the changes which take place when Portland or similar cements are stored is worthy of further investigation. The inherent difficulties of the subject are, however, very serious. The effect of sulfate-solutions (including sea-water) on cement is described later.

Other Factors Influencing the Hydrolysis

Other chemical and physical factors may also exert an important influence on the setting and hardening of cement.

Water. The proportion of cement left unaffected by the water may be important. This depends partly on the fineness to which the cement has been ground and partly on the surface which it presents to the water as a result of the addition of sand or other material which separates the grains of cement. The smallest particles of cement are, naturally the ones most readily affected by the water, but in ordinary commercial Portland cements 30 to 50 per cent usually remains unhydrolyzed in the fully hardened, neat cement. By the addition of sand or other suitable inert material to the cement, the free surface of the latter is increased and the hydrolysis is made more complete. It is important to observe that any unaltered cement takes no part in the hardening (unless it forms a nucleus to the colloid, for which purpose sand of the same fineness is equally efficient). Failure to remember this has led to several fanciful attempts to explain what occurs during the hardening of cements, and has especially led to unnecessarily complex theories as to the reason why a hardened cement will set a second time if it is re-ground and then gaged with water. Careful experiments, with the aid of the microscope, have shown that so long as unaltered cement is present, the hardened mass may be re-ground and re-gaged an indefinite number of times, the limit being fixed by the amount of cement which is hydrolyzed each time the mass is mixed with water. Even with the most finely ground cements and the most carefully made mixtures of these with sand, the whole of the cement is never hydrolyzed the first time the mixture is gaged with water.

Fineness of grinding. The increased rapidity of hardening which characterizes Portland cements which have been very finely ground, is largely due

to the increased surface which these minute particles offer to the water when the latter is mixed with them.

Influence of sand. Many investigations of the hydration of Portland and other cements are based on the compressive strength of the set or hardened product formed when the cement alone is mixed with water. Whilst such tests are often instructive, the fact that they do not develop the full strength of the cement must not be overlooked. This has already been mentioned in describing sand cement (*vide supra*) but its importance can scarcely be overrated. It is obviously wrong to compare the compressive strength of a cement under different conditions in which its maximum strength is not developed, as is always the case when a neat cement is used, because some of the cement then necessarily remains inert. On the other hand, the introduction of an aggregate, such as sand, whilst enabling the cement to fulfill its normal function, also introduces a further complication with a corresponding uncertainty in the interpretation of the results. In practice, the compressive strengths of neat cements are of small value, as it is the strength of the concrete and not that of the cement which is really required and it occasionally happens that one cement which, when neat, gives a lower strength than another, will actually produce a stronger concrete. This very important fact does not appear to have received sufficient recognition in the preparation of the Standard Specifications in use in various countries.

Effect of sulfate solutions, including sea-water. As explained below, sea-water, damp soils or other substances containing any SO_4-ions in solution have a destructive action on Portland cement, causing it to disintegrate and to floresce "as though" (to use Michaelis' vivid phrase) "it had been attacked by a cement-eating bacillus." Candlot's theory that a complex sulfo-alumino-silicate is formed is widely accepted as the cause of the destructive action, but some investigators do not accept this theory. Highly aluminous cements, iron-ore cements, iron cements and blast furnace cements are much less affected by sulfates and are, therefore, used whenever practicable. It has also been claimed that concrete blocks made with Portland cement and cured in an atmosphere of steam are highly-resistant to sulfates. Michaelis and Le Chatelier have both advocated the use of a Portland cement in which a large proportion of alumina has been replaced by iron oxide in places where resistance to sulfates is required.

The chief methods of avoiding the destructive action of sulfates on Portland cements are:

(1) Reducing the lime-content of the cement.
(2) Reducing the alumina-content or increasing it very greatly as in aluminous cements.
(3) Adequately fixing the lime in the wetted cement by adding a pozzuolana such as slag or trass.
(4) Using a waterproof concrete.
(5) Coating the concrete with a protective agent such as bitumen or oil.

Aluminous cements are completely inert to dilute solutions of magnesium sulfate and chloride and, therefore, to sea-water.[117]

NATURAL CEMENTS

Natural cements may be regarded as crude Portland cements and consequently have the same general constitution and properties though their cementitious character is more feeble and their composition more irregular. When a natural cement contains an excess of lime it is intermediate in properties be-

tween Portland cement and hydraulic lime. If a natural cement contains more clay or free silica than can combine with the lime under the condition of manufacture, the surplus silica acts simply as a diluent, reducing the value of the cement. Most of the surplus clay also acts as a diluent but under some conditions, being calcined, it may act as a pozzuolana and so slightly improve the cement.

In the setting of Roman cement an apparently colloidal material is produced by the action of lime-water on the pozzuolana. This acts much more slowly than in the hydration of Portland cements and, consequently, the final hardening takes much longer, though the final effect is the same if the cement is well-proportioned. According to Glasenapp,[118] the magnesia in Roman dolomitic cements forms both a crystalline magnesium hydrate and a colloidal gel.

Hydraulic Limes

Hydraulic limes may be regarded as mixtures of Portland cement and quicklime, and their properties are the same as artificial mixtures of these materials. They are distinguished from Portland cement chiefly by the fact that they slake, or fall to powder, when mixed with a little water, and so do not need to be ground, as does Portland cement clinker. It is, however, important that no more free lime should be present than is essential for this slaking, as an excess of lime merely weakens the cementitious value of the material. Finely ground grappiers are sometimes added to increase the hydraulic properties of the lime.

Hydraulic limes are usually improved by the addition of about 5 per cent of finely ground plaster of Paris and are then known as *Scott's cement,* or *selenitic cement.* The action of the plaster appears to be similar to that of gypsum on Portland cement.

The changes which take place when a hydraulic lime is mixed with water comprise the changes which occur in Portland cement as well as those in lime. Thus, the products of hydration may be the crystalline and colloidal products obtained when Portland cement is hydrated and also either crystalline or colloidal calcium hydrate according to the manner of burning and other properties of the raw materials.

The Setting and Hardening of Aluminous Cements

Aluminous cements of the *ciment fondu* type are made by fusing a suitable mixture of lime and bauxite. There seems to be little reason to doubt that the essential constituent in such cements is monocalcium aluminate, $CaO.Al_2O_3$, which, on hydrolysis forms amorphous or colloidal $CaO.Al_2O_3.xH_2O$; later this undergoes partial crystallization (*vide supra*). Unlike Portland cements, the aluminous ones do not liberate any free lime when wetted.

The hydrolysis of aluminous cements appears to be much simpler than that of Portland cements but very little is known about the cause of the setting. When an aluminous cement is made into a paste with water, the first product of the hydration is, according to Agde and Klemm [119] a series of spherolites and, later, a felted mass. After some time, lime and alumina pass into solution and aluminium hydroxide and silica are precipitated as colloidal gels and bind the mass together. The strongly alkaline solution then recrystallizes.

Aluminous cements, when well made, set slowly but harden rapidly. The hardening is accompanied by a much greater rise in temperature than occurs with Portland cement, so that they can be used with safety in cold and even

in frosty weather. Under normal conditions an aluminous cement is hard enough to walk on, 24 hours after being "placed" and it is usually fit for heavy traffic after three days. The addition of even a small proportion of lime makes aluminous cements set quickly so that care must be taken to avoid adding Portland cement. The setting is also accelerated by nearly two hours if the temperature is increased to 50° C.

To ensure effective hardening and the development of the maximum strength, the wetted cement must be kept saturated with water for at least 24 hours. Fresh water should be used or *dusting* will probably occur,[120] due to loss of water by superficial drying if the mixed material is not kept saturated with water. Sea-water retards the hardening, though the product is more resistant to sea-water than that obtained when Portland cement is used.

The setting is also retarded by the addition of a small proportion of a colloid [121] such as casein, albumen, gum or gelatin, but the use of such substances has other objections and should be avoided. Aluminous cements are almost inert to sea-water.

The Setting of Plaster

The setting of plaster of Paris is now generally considered to be due to the rehydration and formation of crystals of gypsum, $CaSO_4.2H_2O$,

$$2CaSO_4.H_2O + H_2O = 2CaSO_4.2H_2O,$$

forming a mass of long, interlaced crystals which give a certain amount of strength to the mass. The explanation was first suggested by Lavoisier in 1765 and was elaborated by H. Le Chatelier [15] who showed that when the hemi-hydrate (plaster) is dissolved in water it forms an unstable solution supersaturated with gypsum which, being less soluble, crystallizes around nuclei of unburned particles in radial form, the needle-shaped crystals interlocking and forming a strong mass. The process is not carried to completion on account of insufficiency of water, but the grains of hemi-hydrate are covered with a layer of matted crystals which unite them together into a strong mass. The water liberated when the dihydrate is precipitated continues to dissolve further quantities of the hemi-hydrate and so the action continues.

During the setting the temperature rises considerably and the volume is increased by about 20 per cent. The cohesion of the mass is attributed to the extremely elongated shape of the crystals and the manner in which they form a felted mass; this is confirmed by the fact that if, by prolonged mixing, the needles are broken into small pieces, the strength is reduced so much as to make the plaster useless.

The presence of nuclei around which the crystals can form appears to be essential as when plaster is hydrated and set with pure water, crystals are not discernible; they begin to develop after a few weeks. When alcoholic water is used, or an accelerator is added, the crystals form much more rapidly.

Cloez [112] found plaster to be hydrated in two stages as evidenced by two distinct rises in temperature and the density of the hydrated plaster being different from that of definite hydrated calcium sulfate. This has been confirmed by Chassevent [123] who attributed it to (*a*) the hydration of the anhydrous sulfate to form the hemi-hydrate and a saturated solution causing the first rise in temperature, and (*b*) the crystallization of the dihydrate and further solution of the hemi-hydrate which immediately crystallizes, causing the second rise. From an investigation of the variations in the electrical conduc-

tivity of the solution in the immediate vicinity of the plaster Chassevent [124] concluded that plaster of Paris prepared below 300° C. is transformed immediately on contact with water into the hemi-hydrate, forming a solution which is supersaturated with respect to gypsum. Later, gypsum crystallizes and heat is evolved; simultaneously setting occurs. Setting is accelerated by salts which increase the concentration of the sulfate ion and by acids which do not cause a precipitate.

It would appear that the hydration is not free from complexity and Davis [125] has suggested that the dihydrate is dimorphous, a rhombic form first crystallizing and later being converted into the stable form. Rohland [126] suggested that the setting of plaster was due to water being taken into the salt in the colloidal form, thus causing caking. He uses this explanation to explain the caking of other salts, but it has not been generally accepted on account of the lack of evidence. Ostwald and P. Wolski [127] have stated that the changes in viscosity of dilute (2 to 5 per cent) suspensions of plaster when examined in an Ostwald viscosimeter show that colloidal phenomena play an important part in the setting and hardening. They found the viscosity-time curve to be S-shaped, the viscosity rising slowly at first, then more rapidly and finally becoming constant at its maximum value. Desch's theory [130] of crystal thrust appears to explain the differences in expansion on the setting of plaster of Paris, gypsum cements and anhydrite.

Under ordinary circumstances it is necessary to avoid using a large excess of water, but if pressure can be applied to the plaster whilst it is setting—as when making plaster molds for Marseilles tiles—a much "wetter" mixture may be used and a denser and harder product obtained.

A curious phenomenon has been discovered by Krauss,[128] who found that if the vapor pressure and temperature curve of gypsum starting at 7 mm. pressure is plotted, there is a large part of the curve where no pressure is shown, but suddenly at 73° C. a pressure of 24 mm. is produced. If the mixture is cooled to 0° C. and the experiment repeated the gypsum is converted into the hemi-hydrate at 59° C., whereas with ordinary gypsum a temperature of 107° C. is required for the conversion. This suggested an unsuspected complexity in the constitution of gypsum and, therefore, in its behavior when mixed with water.

Accelerators and Retarders. It has long been known that the speed of setting of plaster of Paris can be increased by various salts such as sodium, potassium, magnesium and ammonium chlorides, sodium, aluminium and potassium sulfates and by prolonging the mixing. Haddon and Brown [129] have found that the speed of setting may be varied by altering the amount of hemi-hydrate and the sizes of the particles. It also depends on the manner in which the plaster has been "boiled" or "burned" as over-burned plaster (i.e., totally dehydrated gypsum) sets very slowly on account of the slowness with which it dissolves in water; when it finally sets it attains a great hardness.

Haddon and Brown regard Rohland's theory that the catalytic effect of other salts on setting is proportional to their effect on the solubility of calcium sulfate as untenable. The setting of plaster of Paris is retarded by the presence of calcium chloride, borax and various colloidal materials such as glue or casein which coat the particles of plaster and prevent them from dissolving so readily.

The action of accelerators and retarders has been summarized by Rohland [131] who suggests that accelerators increase the solubility of the gypsum, whilst retarders reduce it. The *hardness* of plaster of Paris may be increased

by mixing with alum or some other accelerators; these form the basis of Keene's cement and other proprietary cements and plasters.

The *strength* of plaster of Paris, when set, is chiefly due to the extent to which the crystals interlock and form a felted mass, but it may also be due, in part, as suggested by Haddon and Brown,[130] to the adhesion of the crystals to each other in a similar manner to the strength of metals.

Oxy-Acid (Sorel) Cements

Oxy-acid cements appear to set in the same manner as plaster, the strength being due mainly to the interlocking crystals produced by the chemical reaction. Thus, zinc oxide and zinc chloride give a highly super-saturated solution from which zinc oxychloride slowly crystallizes.

Magnesium oxychloride cements are usually supposed to set in a manner similar to plaster, but Kallauner [132] suggests that the setting is more probably due to the formation of a solid solution of magnesium hydroxide and magnesium chloride, seeing that the latter is readily removed by alcohol.

If colloids play any part in the setting it would appear to be very small, though the short period of placticity which occurs before setting takes place appears to indicate the presence of colloidal material. Up to the present, however, no evidence has been considered satisfactory which requires a colloidal theory.

Mortars

Lime mortars. The chief ingredients used in the production of lime mortars are not usually colloidal. The sand is composed almost wholly of fragments of crystals of quartz and the lime, whilst amorphous, does not show any marked colloidal properties in its dry state. On bringing it into contact with rather more water than is required to form calcium hydrate, slaked lime behaves in many respects as though it were a colloidal gel, possessing most of the properties characteristic of colloids. As calcium hydrate is only slightly soluble in water, it rapidly forms a supersaturated solution from which the crystalline hydrate may separate in long needle-like crystals and may eventualy form a fibrous mass, though most of the calcium hydroxide in set lime mortars appears to be structureless; it may, however, be either colloidal or minutely crystalline. In time, recrystallization may take place, but the crystallization is not an essential part of the initial hardening as most of the strength is obtained in a comparatively short time. It would thus appear that the main cause of hardening is the formation of a calcium hydrate gel which cements the grains of inert sand and encloses any crystals of calcium hydrate which may be produced.

The cause of the later hardening of ordinary mortar is due solely to a further reaction, namely, the absorption of carbon dioxide from the air with the production of calcium carbonate in the mortar. It was, at one time, supposed that the lime and sand combined with each other, at least superficially, but numerous examinations of very ancient * as well as more modern mortars has clearly shown that such combination only occurs (if at all) to a negligible extent. Other investigations on the combination of lime and silica have shown that a temperature of at least 240° F. (115° C.) is required before any noteworthy amount of combination can occur. The fact that, when an ordinary lime mortar is kept in an atmosphere free from carbon dioxide,

* Many ancient mortars contain pozzuolanic material with which the lime can combine chemically (vide supra).

no hardening occurs, appears to be sufficient proof that carbon dioxide is an essential constituent of hardened mortar.

When mortar is used in brickwork a further cause of hardening may sometimes be observed, namely that due to a combination of the calcium hydrate with the finer particles of burned clay on the surface of the bricks. Such a combination closely resembles that of lime and pozzuolana, but the very limited area of fine particles of burned clay exposed to the action of lime makes this form of hardening of very little importance. By using the burned clay in a more accessible form (as when very finely ground brick dust replaces some of the sand in the mortar) a considerable increase in the strength of the mortar is produced. In ordinary bricks and mortar which have been united for very many years, there is usually a hard, thin film of combined material at the interface between the bricks and mortar. The use of *diatomaceous earth* in a mortar (replacing part of the sand) increases both the workability and strength of the mortar—probably because the silica in the diatomaceous earth can combine chemically with the lime. *Clay* should not be present in ordinary mortar as it tends to coat the particles of lime and prevents them from adhering properly to the sand.

In all sand-lime mortars, it is essential that the proportion of water should not be excessive and that the action of the carbon dioxide should be exceedingly slow or the mortar will not harden. Thus, mortar which is exposed to carbon dioxide gas instead of air will form a crystalline calcium carbonate with little or no hardening properties and the mortar will fail to serve its true purpose.

Hydraulic lime mortars owe their increase in hardness to the cementitious matter other than lime which they contain. The lime hardens superficially as described in the section on Lime Mortar, whilst the cementitious matter hardens like Portland cement. As lime in such a mortar can never harden completely, a hydraulic lime mortar is inferior to a cement mortar, but superior to a fat lime mortar.

Cement mortars. These mortars harden precisely like cement, and owe their hardness solely to this constituent. They are greatly improved by the addition of trass (*vide supra*) or a small proportion of sand of the same fineness as the cement.[133] Lindmann [134] states that mixing finely ground glass with cement clinker produces an increase in the tensile strength of the mortar. On the other hand, the presence of loam containing vegetable matter (or tannic acid itself) weakens cement. As little as 0·1 to 0·5 per cent of tannic acid has a very serious result on the strength of a cement mortar. A well-made cement mortar has many of the properties of a colloidal gel. It expands and contracts according to the humidity of the atmosphere and flows gradually when under load with a plastic movement, which is not reversed when the load is removed. These movements and their extent, as well as the chemical and physical changes that occur in the setting and hardening of cement mortars require to be known more intimately than they are at present.

The correct proportioning of the materials and especially the cement-water ratio is of paramount importance, as Abrams [87] has shown that an increase of water beyond the optimum gives a reduced strength. This is confirmed by Weisgerber [135] who has found that the maximum strength is not dependent on the consistency of the mixture but is a function of the cement-water and cement-sand ratios and, therefore, of the composition of the mortar.

The consistency of a mortar depends on (1) the proportion of water used in mixing; (2) the sizes of particles of the solid ingredients; (3) the chemical and physical nature of the cement and aggregate, and (4) the temperature and

degree of aeration of the aggregate. The consistency which produces the maximum density also gives the maximum strength and minimum permeability, but such a mixture is usually too stiff to work well. Far too little attention appears to have been paid to the cement-sand ratio and the empirical use of 1 : 3 or 1 : 6 mixtures is to be deprecated.

The concrete paste is the true basis of quality and a mortar should not be made by merely filling the voids of the sand or other aggregate with the grains of cement but as a process of preparing a cement-sand paste of a plastic, homogeneous, workable nature. The sand or other aggregate must be carefully graded so as to produce a workable mixture with a minimum of water. A cement-mortar should not be finer than is necessary or it may shrink too much. The grading which gives maximum strength also makes impermeable mortar. Careful manipulation is essential for best results. Homogeneity and a proper degree of workability (plasticity) are essential to a proper placing of the mixture without segregation.

The quality of a cement-mortar is best assured by weighing all the materials used, as this eliminates variations in bulk and grading and simplifies the production of a correct cement-water ratio. Bates has emphasized the importance of thorough packing and working the mixture as a means of securing density and homogeneity and of preventing cracking, but excessive mixing must be avoided. The strength of a cement-mortar may be increased by the addition of trass or other pozzuolana if there is not too much fine material present, but an excess of fine material leads to loss of strength. The most serious defects in cement-mortars are cracking, crazing and dusting.

Cracking is usually due to the use of too much water or too much cement or to a wrong cement-water ratio, but it may also be due to the mortar having a coefficient of expansion different from that of the surface to which it is applied.

Crazing [136] is due to too rapid evaporation from the surface of a rich cement-mortar before it is fully hardened. The surface contracts on drying and hair-cracks are caused through the difference in tension between the surface and the body of the mass, whereby the water-molecules are drawn together. Dryish mixtures are, therefore, less liable to craze than those which are very wet.

Dusting is a form of decomposition which results in the formation of a light dust on the surface of the articles made of concrete. It may be due to several causes, the two most important of which are: (a) the presence of dicalcium silicate, $2CaO.SiO_2$, in the Portland cement, and (b) insufficient water in the concrete, particularly during the first week after it has been made. The first cause is due to a defect in the manufacture of the cement; the second is usually due to not keeping the concrete sufficiently damp during the curing process.*

When once the material is properly hardened and is subsequently wetted, the rapidity of the drying does no further harm. In some cases, however, the colloidal material present retains its colloidal nature for many months and the stresses caused by alternate drying and wetting increase as the amount of colloidal material increases and may result in structural cracks. Crazing may usually be prevented by using lean mixtures and keeping the moisture-content constant until sufficient hardening has occurred. The conditions and duration of curing have much greater influence than other variables and water-tightness is also influenced by the cement : water ratio.

*** Asphalt emulsions (*see* index of this volume) are being largely used in "seasoning" cement roads, etc., for they prevent drying out and dusting. J. A.**

Cement-lime mortar. This is a mixture of cement-mortar to which slaked lime has been added. The lime greatly improves the "workability" of the mortar, but Johnson[137] has found that it increases the amount of water needed and so increases the shrinkage of the mortar. The addition of lime increases the strength of cement mortars leaner than 1 : 2 by weight; it also increases the density and shortens the time of setting as well as increasing the plasticity or ease of working.

Cement-trass mortars. These mortars owe their hardness (*a*) to the cement and (*b*) to the combination of the trass with the lime set free when the cement is wetted, an additional quantity of an insoluble cement being thereby formed. The result is that cement-trass mortars are more resistant to water and are more durable than any other. When possible, the cement and trass should be ground in a dry state prior to mixing them with the sand or concrete. As the mixing should be very intimate, it would be best done at the cement works.

Clay mortar. This mortar hardens on drying in precisely the same manner as other colloidal gels (clay having marked colloidal properties), but on exposure to water it is again softened and may be washed away. Consequently, clay mortar cannot be used where resistance to water is essential. (In arid regions *adobe* is often used for houses. J. A.)

When clay mortar is used in furnaces or other structures which are heated to temperatures above 600° C. the clay is decomposed and a hard, stony product is formed, the hardness increasing with the temperature and duration of heating. In this respect, clay mortar differs from all others, as the hardness is not caused by the chemical combination of two or more substances, but by the decomposition of the clay. Any sand or grog present in the clay mortar remains inert; its chief function is to reduce the shrinkage of the mortar which would be excessive if clay alone were used.

Water-proof Cement Mortars

Many attempts have been made to produce siliceous cement mortars which will be water-proof when in use, but although many of these materials may correctly be described as water-resisting, few, if any, of them are completely water-proof under all circumstances. They consist chiefly of (*a*) *pore-fillers* such as alum, trass and other pozzuolanic materials, silica flour, fluosilicates, water-glass and lime soaps. Some of these combine with the lime set free when the cement is wetted and so prevent it from being washed out of the mortar; others merely fill the interstices and prevent the entry of water, and (*b*) *protective coatings*, applied to the surface of the mortar, such as paint, tar, bitumen or emulsions of a water-resistant character. These coatings may be completely water-proof so long as they last, but wear away in course of time. A. H. White has pointed out that tests of the water-proofness have usually been made on the material with any colloid present in a fully swollen condition. A cement mortar which is properly made of a fairly rich mixture and thoroughly hardened under water will not permit any water to pass through it because the swollen colloid closes all the capillary pores, but if the wet mixture is exposed to the air, the free lime in it is dissolved in the water and a saturated solution of calcium hydroxide travels to the surface of the block. This becomes converted to calcium carbonate through reaction with the carbon dioxide of the air, and the calcium carbonate thus deposited seals the capillary openings. In this way, the surface of a fairly rich mortar, which is alternately wetted and dried, will water-proof itself in time through deposition of calcium

carbonate. The water-proofing will, however, reside mainly in the skin and the center of the mass will still have capillary openings.

The most impermeable mortars are those in which the proportions of the various ingredients are such as to produce a minimum of voids or interstices between the solid particles. This can only be obtained by carefully grading or sizing the particles and then, starting with the largest, adding sufficient of each smaller size in succession to fill the interstices between the larger particles. The volume of the interstices may be found by determining the volume of water which can be added to a given volume of the material without increasing the volume of the latter.

The addition of soaps, fluorides, fluosilicates, water-glass and the like, and other water-proofing agents, whilst quite successful for many purposes, does not fulfil all the requirements of a water-proof cement.

Acid-resisting Cements

Although many attempts have been made to produce an acid-resisting cement of a similar constitution to Portland cement, no completely satisfactory results have yet been obtained.[138]

Curing Cements and Mortars

In course of time, cements and mortars increase in strength, the greater part of their strength being obtained fairly rapidly, though the maximum may not be obtained for many years. In the case of fat lime mortars, little can be done to increase the strength, as this is almost wholly due to atmospheric hardening, but the time taken to approach the maximum hardness may be greatly shortened by suitable methods of curing.

The most important methods of curing all cement mortars are:

(a) Keeping the mortar wet until the whole of the cement in it has become hydrolyzed and the resulting materials have been supplied with as much water as they require. For most purposes, it is sufficient if the material is kept thoroughly wetted for a week. One means of doing this, consists in covering the exposed surface of the mortar with a layer of finely ground calcium chloride which will act as a source of water and will supply it to the mortar by capillary attraction. The use of calcium chloride for this purpose has greatly increased during recent years, especially in road construction.

(b) By keeping the mortar in a moist atmosphere at a temperature of about 70 to 150° F. This is inapplicable to many mortars but is extensively used for curing molded articles made of the same materials such as window sills, finials and blocks of "artificial stone."

(c) By keeping the mortar covered with wet cloths for 24 hours and then applying a solution of water glass of 36° to 37° Bé or a specific gravity of 1·33 to 1·34.

Concrete

Most of the properties of concrete are closely allied to those of cement mortars, though the presence of a coarse aggregate modifies them to a considerable extent. Instead of regarding concrete and cement mortar as quite distinct, it is being increasingly recognized that concrete is a cement mortar with pieces of inert, coarse material embedded in it and that the properties of the whole mass depend chiefly on those of the mortar. Concrete should, therefore, be cured in the same manner as cement mortars.

Future Developments

As the useful properties of cements are essentially of a physical character, a more intensive study of the "colloidal" properties of wetted cements appears likly to be of great value. Such a study is equally applicable to the highly aluminous as well as to the highly siliceous cements. For this purpose, an investigation of the properties of cements which have been made of purer materials, burned more uniformly and ground much more finely than the ordinary commercial materials is also desirable. The effect of grinding the cement with a suitable proportion of trass or other pozzuolana should be investigated.

To obtain an ideal Portland cement on a large scale is not yet possible, but each year a nearer approach is made to it. Theories based on the colloidal properties of wetted cements and also on the structure of amorphous solids point to the possibilities of great increases in strength resulting from further investigations on the temperature of burning, the rate of cooling and the fineness of grinding of the clinker, as well as of the true nature of the cement both in the clinker and hardened states. The field of such problems is extremely large; the investigations made hitherto are only at the threshold, and it remains for younger men to face these problems aided by a broad outlook and strengthened by a great hope.

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The Colloidal State in Metals and Alloys *

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The fact that the order in which atoms or molecules of the same kind are assembled may profoundly affect the chemical and physical properties of the resulting mass, is clearly demonstrated by allotropy. Consider, for example, the strikingly different properties of yellow, red and black phosphorus; of γ and μ sulfur; and of graphite, the lubricant carbon, and diamond, the hardest known substance. Since the basis of allotropy involves a special arrangement of atoms in a space lattice, obviously only a *group* of atoms can exhibit it, and the question naturally arises as to *how small* a group can form a particular allotrope which would be stable under a given set of conditions. It would not be surprising if such a minimum size group would, under some conditions, be of colloidal dimensions. This seems to be the case in the transparent rubber-like elastic sulfur formed by suddenly chilling this element from its upper range of fluidity.

The enormous strides made by chemistry in the last century centered attention upon the *chemical* composition of materials. But great as is the information given and the service rendered by chemistry, scientific investigation has made it increasingly evident that the *structure* of a substance is also of marked, and sometimes of paramount, importance in determining its practical working properties—a fact well known and made use of by artisans and mechanics. Chemical analysis of a loaf of bread tells much, but does not evaluate its lightness, freshness, or saleability, nor is a chemical analysis of steel an index of its practical working properties.

The pioneers of colloid chemistry saw more or less clearly that molecular aggregation is an underlying basis of colloidality. Thus Thomas Graham ("On the Properties of Colloidal Silicic Acid and other Analogous Substances," *Proc. Roy. Soc.* (*London*), June 16, 1864) wrote:

"The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule."

Many others, e.g., Sir William Ramsay ["Pedetic Motion in Relation to Colloidal Solutions," *Chem. News,* **65**, 90 (1892)], M. Carey Lea, Carl Barus, also saw the relation between particle size and behavior; but it was the discovery of the ultramicroscope by Richard Zsigmondy (1903) and the subsequent investigations made with it, that demonstrated *visually* that, with decreasing particle size, the Brownian motion seen in particles at the lower limit of ordinary *microscopic resolvability* (about ¼ μ) increases rapidly, until in particles at the lower limit of *ultramicroscopic visibility* (about 5 mμ), it becomes enormous in speed and amplitude. Investigations by A. Einstein,

* An extensive bibliographical review of recent papers dealing with colloid aspects of metals is given by R. E. Liesegang in *Kolloid-Z.*, **49**, 332-343 (1929).

M. Smoluchowski, J. Perrin and others proved that the motion seen was a visual confirmation of the kinetic theory, for it corresponded with the kind of motion calculated for particles of these sizes, thus justifying the surmise of Ramsay (*loc. cit.*) that "a continuous passage can be traced between visible particles in suspension and matter in solution."

This made evident the point stressed by The Svedberg, P. P. von Weimarn, and others, that the colloidal degree of dispersion can be reached either by the *aggregation* of atoms, molecules, or other ultra-colloidal particles up to a colloidal degree of largeness, or else by the *dispersion* of supra-colloidal particles down to a colloidal degree of smallness. In fact in dispersing from visible particles to solution, any substance must to a greater or less extent pass *downward* through the colloidal range of dispersion (roughly 100 mμ to 5 mμ); and conversely, any substance coming out of solution (whether by chemical or physical precipitation or separation) to form visible particles, must likewise pass *upward* through the colloidal zone. But it very frequently happens that conditions prevent the emergence of the substance from the colloidal zone, and there it remains, forming a colloidal dispersion.

Since colloids may be formed by aggregating crystalloidally dispersed particles or by dispersing relatively coarse particles, J. Alexander [1] pointed out that there must be a *zone of maximum colloidality* within the range where the effects of increasing free surface per unit of mass (specific surface) acquired their greatest potency, just before rapidly increasing kinetic activity acquires dominance and produces true or crystalloidal dispersion or solution. Naturally if the molecule itself is of colloidal dimensions, molecular dispersion is colloidal dispersion. The zone of maximum colloidality has been considered at length in the first paper in Volume I of this series, and phenomena due to its existence occur in metals and alloys. But it must be remembered that it is a phenomenon of general occurrence, and may be exhibited by any substance, metallic or non-metallic.

Historical.

As so frequently happens, the colloidal aspects of metals and alloys have been independently noted by different investigators at different times. So far as I at present know, the first to refer directly to the colloidal behavior of metals was Dr. H. Kneebone Tompkins, whose thesis, written in 1896, was published only in 1921 as an Appendix to the report of a joint meeting of the Faraday Society and the Physical Society of London, held Oct. 25, 1920. Dr. Tompkins' paper is entitled "On the Internal Pressure of Liquids."

After referring to the analogy between vulcanized caoutchouc and colloidal sulfides, gelatin, wool and cellulose (*loc. cit.* p. 184), Tompkins says:

> "There seem to me to be very good reasons for regarding the metals as colloids, amongst which are their malleability, ductility, and elasticity. The slow softening which some of them undergo when heated, the absence of any definitive molecular weight (Dulong and Petit's law refers to the atom), but most of all the nature of metallic solutions. If a piece of tinned copper be placed in molten tin at a definite temperature, some of the copper dissolves in the tin and the latter probably dissolves to a certain extent in the solid copper. If the temperature be raised, greater quantities dissolve and finally the two metals mix completely, forming a homogeneous liquid. If now the mixture be cooled, the copper does not crystallise out but the two substances generally set as a whole. This behaviour distinguishes the alloy from all solutions of crystalline substances, but not from solutions of colloids such as gelatin. For if the latter be placed in water it swells to a certain extent. If the temperature be raised more water passes into the colloid, and finally when the colloid is 'melted' it mixes in all proportions with the water. Now, if the solution be cooled, no separation of the gelatin and water takes place but the mass sets as a whole; so that we have here a complete analogy if we consider the copper as being

sometimes a colloid. It may be noted that the most malleable metals are those which crystallise in cubes. With three equal axes, the confused arrangement representing a colloid would probably be most easily produced. . . .*

". . . Now those substances which are most injurious to iron, viz., sulphur and phosphorus, are those which can mix with it in all proportions, and which therefore have a large affinity for iron and would be able to produce a large distension. Moreover, we see that the effect of any one element will be influenced by those already there. . . .

"In the rubber experiments the constituents inside the colloid are balanced by those outside. This is probably also the case when the metal is submerged in the impurity-giving slag. On cooling some of the constituents may crystallise out. These would be considered to be external to the metal. That such a balance between fluid mixture inside and fluid mixture outside the metal really exists, at any rate when the metal is red hot, is proved by the experiment of M. Lencauchez (Roberts-Austen's "Introduction to Metallurgy," p. 74), in which iron was maintained at a red heat for 100 hours in order to allow fluid constituents to diffuse out. At the end of the experiment the metal was found to be coated with grains of slag which had sweated out, the following being the composition inside and outside the metal.

	Iron	Slag
	Per Cent	
Phosphorus	1.9	4–6
Silicon	2.6	0.6–0.8
Graphite	3.5	0–1.5
Combined Carbon		0–1.24

"If the exuding fluid were continually scraped off a simple method of removing phosphorus would be the result, but it would be a very slow one.

"Another fact bearing on the idea of a constituent, so dilute as to be 'gaseous,' acting in opposition to the volume elasticity of iron, is the statement of Roberts-Austen that the tensile strength of electrolytic iron containing 250 times its volume of hydrogen is only 2.7 tons per square inch, whilst after annealing it rises to 15.5.

"There are necessarily many considerations which will modify the final result, but it seems to me that it is only by some such theory as the above that it is possible to account for the extraordinary effect which is in some cases produced by small quantities of substances dissolved in iron. . . .

"Another property of metals of wider application is the change in tenacity produced by the addition of very small quantities of other elements and which depends only upon the atomic volume of the added element. . . .

"If the added element has an atomic volume greater than that of iron, the tenacity of the latter is increased, and it assumes the hard dense 'α' modification. On the other hand, if the dissolved element has an atomic volume less than that of iron, the tenacity is decreased and the iron is found to be in the soft less dense 'β' condition. This change of tenacity is not confined to iron but has been shown by Roberts-Austen to apply equally well to gold and other metals, and it is brought about by very small proportions so that it cannot depend upon the mutual attractions of the 'foreign' atoms for one another, but is determined solely by the volume of the atoms relative to those of the metal in question. . . .

"Since colloids may be looked upon as liquids which have failed to crystallise, and may be considered to have many of the properties of liquids, the above considerations may perhaps be applied generally to liquids and concentrated solutions. . . .

"Another property of metals which may be explained by the application of van der Waals' equation to dissolved substances is liquation. When a mixture of metals is cooled a partial separation takes place after solidification and the constituent of lowest melting-point is always found to have travelled in towards the centre. The same is found to be the case with the non-metallic impurities in iron. Now I have considered the outward pressure of a dissolved substance to be $p - ap^2$, or more fully $p - (a - A)p^2$, where ap^2 is the inward pressure due to the attraction of the atoms of the dissolved substance for one another, and Ap^2 the outward pressure due to the attraction between the substance and its solvent—a being always greater than 'A'. Now, as the temperature falls the outward 'gas'-pressure 'p' decreases and the whole expression becomes negative, the result being that the still fluid constituents will be drawn inwards. As the force 'A' is due to the mass of the solvent, its effect will be to direct the condensing substance towards the centre of gravity of the mass.

"If the metal be cooled with extreme slowness, liquation takes place to a much less

* The contrary is generally true. Irregularly shaped, polar molecules are prone to form colloidal groups. J. A.

extent, which may perhaps be explained by supposing that the solvent mass crystallises. Diffusion through its mass might then be impossible, since there is no tendency for crystalline solids to diffuse into one another, nor for a liquid to diffuse through a crystalline solid.* Solids, on the other hand, will diffuse into colloids. Thus, Sir Frederick Abel has shown that a highly-carburised iron plate will lose carbon to a non-carburetted one even at the ordinary temperature if they are tightly pressed together. Again, solid sulphur will diffuse easily into caoutchouc. The above explanation of liquation would perhaps apply to the separation of flints in chalk, especially as the alkalies in the soil would render the siliceous debris somewhat soluble. As the molecular weight (or volume) of gelatinous silica is very great, the separation would be very slow.

"In connection with the diffusion of colloids into colloids, it would be interesting to see if colloidal sulphur will vulcanise caoutchouc more rapidly than the crystalline element.

"Analogy between the Action of Dissolved Substances on Swollen Colloids and on Freezing Liquids.

"It is usually considered that a liquid in the act of freezing is not homogenous. In some parts of it the molecules are brought together sufficiently closely that they are in the act of forming crystals; in other parts this is not the case. If the molecules forming the 'nascent' crystals be considered to represent the colloid in the above experiments, and the other portion of the freezing liquid to represent the fluid surrounding and penetrating the colloid, the first effect of the addition of dissolved substances to the freezing liquid will be to drive asunder the crystal formed molecules, just as dissolved substances at first expand rubber; and from the above experiments the amount of separation will at first be equal for equal numbers of molecules of dissolved salt. The temperature must then be lowered, in order that the crystals may again begin to form; and since the separation of the crystal molecules is equal for equal numbers of molecules of dissolved salt, the lowering of temperature required will also be equal. This analogy between a colloid and the confused agglomeration of molecules representing a 'nascent' crystal is rendered more reasonable if we consider a colloid to be intermediate between a liquid and a crystalline solid. The crystallisation of a colloid may either never take place or it may be postponed.† The latter condition may apply to metals, and the imperfect separation of copper on cooling a solution of the metal in tin may be due to a tendency of the metal to crystallise: if it were a true colloid, the metallic mixture should always solidify as a whole. The crystallisation of steel under continued concussion would point to the same conclusion, viz., that the crystallisation has been postponed. Colloids, as we have seen, allow substances, both solid and liquid, to diffuse through their mass, and thus resemble liquids. Crystalline solids, on the other hand, do not allow of any diffusion through their mass. This is probably due to the short range of forces which bind together the molecules of a crystal. If, for instance, ice be brought into contact with salt, there is probably an affinity between the two substances, just as there is between caoutchouc and carbon bisulphide; but in one case the molecules are torn asunder and separated from one another, the result being that there is a change of state and consequent great absorption of heat: in the other case the solid is simply submitted to a strain, and little or no heat is produced. That this is the case was proved by placing a piece of rubber tubing lightly over the bulb of a thermometer and immersing it in carbon bisulphide. No change of temperature took place. The fact that the heat of 'solution' of colloids is practically nought is in favour of the view which has been put forward, viz., that colloids do not readily dissolve, i.e., separate into chemical molecules, but that the volume elasticity of the solid is simply infinitely strained."

The X-ray spectrometer indicates that while colloid particles are often crystalline (the "nascent" crystals envisaged by Tompkins), such particles may also consist of random groups, not regularly arranged in a space lattice. Indeed, as P. Scherrer's X-ray spectrographic investigations of silicic acid and stannic acid sols revealed, crystalline and non-crystalline colloidal particles may co-exist in the same dispersion, the tendency being for the non-crystalline groups to become crystalline on ageing. Mesomorphic groups (G. Friedel ‡) must also be considered where they exist.

* Roberts-Austin placed lead and gold slabs in contact and found that the metals *very slowly* diffuse into each other. Case hardening depends on diffusion. See also first paper in this volume. J. A.

† At this time it was not clear that colloidality depended merely on particle *size*, and that colloidal particles may be crystalline. Particle size is a powerful factor even though transformation to a new X-ray space lattice occurs. J. A.

‡ See his paper in Vol. I of this series.

But irrespective of the orientation of its constituent molecules, *whenever a particle reaches a certain size, its kinetic activity is markedly reduced.* In the competition for molecules which emerge from solution (e.g. by compound formation, by cooling or evaporation of solvent), such "corpulent" particles would tend to grow at the expense of smaller particles which present much more surface per unit mass, are much more active kinetically, and are therefore more soluble.* Besides this, slow-moving particles may aggregate (agglomeration, flocculation, coagulation) into larger groups wherein their individuality may be preserved by chilling or by the presence of inhibiting substances intentionally added or often present as impurities.[2]

A simple experiment will illustrate the simultaneous coexistence of all these possibilities.

Some Canada balsam is added to a solution of sulfur in carbon bisulfide, in order to yield, on evaporation of the solvent, a viscous medium which will hamper the normal crystallization of the sulfur. A drop of this mixture is rubbed out on a microscope slide, and dried almost instantaneously by blowing on it. On examining slides of this kind the microscope and ultramicroscope (dark field), areas will be found which exhibit the following phenomena:

1. Scattered spherulites, apparently formed by aggregation of ultramicroscopic crystals (*crystallogens*) into spheres by surface tension forces. When these crystallogens reach the lower limits of colloidal dimensions, their kinetic activity diminishes sharply, and aggregation becomes possible.
2. Grouped spherulites. Most of these will be found in margaritic or dendritic groups, but may also occur in more compact, crystal-like masses in which they still preserve their individuality. The groupings are obviously consequent upon the polarity of the spherulites, which in turn is due to their free fields of force.
3. Definite sulfur crystals. When the molecules in the aggregated spherulites snap into a single continuous space lattice, a single sulfur crystal results, and it is usually surrounded by a vacant space which it has cleared of spherulites. Occasionally, in the dark field, isolated ultramicrons can be observed along crystal edges, probably representing small molecular groups which, when the rearrangement occurred, could find no place in the space lattice.

Analogous phenomena occur in metals and in alloys, but in them, on cooling, the "solvent" may form aggregates in addition to those formed by the dispersed substance.

Much regarding the minute structure of metals may be determined by metallography, which involves the microscopic examination of suitably polished and etched metallic surfaces. Metallography has been most fruitful of results, and much of our present knowledge of metals and alloys has been attained with its aid, particularly knowledge of the crystalline phase or "grain." Of the so-called amorphous or colloidal phase, however, metallography can tell us but little outside of its occurrence and distribution. Owing to the great opacity of solid metals, it has thus far been impossible to subject the colloidal phase to successful ultramicroscopic examination, and such examinations of thin films along the lines laid out by Beilby present difficulties and cannot apply to the mass, although they may be of interest.

Similarities Between Hot Glass and Hot Metal.

But glass may be readily examined ultramicroscopically, and a consideration of the phenomena observed in glasses will serve for the present to give some insight into what occurs in metals and alloys.[3]

* See paper by Geo. W. Hulett, p. 637, Vol. I of this series, entitled "Solubility and Size of Particles."

Among glass technologists a molten batch of glass is termed "metal," a term remarkably well chosen, for, strange as it may appear, there are numerous analogies between glasses and most metals. Both are produced or fused at high temperatures, and as they issue from the furnaces are, for the most part, heavy viscous liquids [4] prone to set and crystallize. Both exhibit the phenomena of supercooling to a marked degree if quickly chilled. Both may be cast, molded, pressed, drawn and annealed or tempered—they are in fact thermoplastic and their physical properties are largely dependent upon their thermal and mechanical histories. There are, of course, many enormous differences between glasses and metals, and very marked differences exist even in their analogous properties. Thus with metals the crystallization tendency is powerful and quick acting, whereas with glasses the composition is generally chosen so as to prevent crystallization under operating conditions, some of the constituents of glass apparently serving as protectors or inhibitors of crystallization toward the others. Furthermore, metals tend to cool much more rapidly than glasses because of their greater thermal conductivity; but their rapid crystallization usually outstrips their chilling, notwithstanding the fact that the latter is often facilitated by quenching.

Behavior of Supercooled Melts.

As Tammann has shown,[5] there are three main factors which control the behavior of supercooled melts: (1) The specific crystallization capacity (which is measured by the number of centers of crystallization formed in a unit mass in a unit time); (2) the speed of crystallization; (3) the variation in viscosity. In the case of the various mixtures of fused silicates composing molten glasses, the viscosity increases so rapidly upon cooling that the crystallization forces are unable to establish themselves before the melt becomes too rigid to permit molecular orientation. The result is the amorphous, or colloidal, mass we call glass. In very quickly cooled glass—i.e., Prince Rupert bubbles—the internal strains are so great that the glass is actually explosive; and in the ordinary process of manufacture glass has to be annealed to render it less brittle. This is accomplished by cooling the glass very slowly, keeping it at a low heat for a long time so that there may be a partial adjustment of the aggregation tendencies of its particles. Gelatin jellies act similarly, but, because of their softness, anneal spontaneously at room temperature.[6] Thus F. Stoffel [7] has shown that quickly cooled gelatin jellies permit the more rapid diffusion of electrolytes than slowly cooled jellies; but the difference equalizes itself after several days. Incidentally this shows the higher dispersion of the particles in the quickly cooled jelly and the greater total area of diffusion paths; but the average cross section of the paths would be less.

If the composition or heat-treatment of the glass is such that crystallization occurs, we call the phenomenon devitrification—the glass becomes cloudy or opaque. The inherent tendency toward crystallization exists even in clear glasses, and may be realized after a very long lapse of time. The composition of opaque glasses is so chosen that under usual conditions a turbidity is produced, a fine precipitate which renders the glass opaque. James Gillinder, of Port Jervis, N. Y., was kind enough to make for me some Prince Rupert drops from a batch of opal glass. The exterior rind of the drops was clear or showed a faint turbidity, whereas the interior, which was of course more slowly cooled, was milky and opaque. At the surface the chilling was from

about 1,200 deg. down to 15 or 20 deg.* Thus ancient Egyptian and Roman glasses are frequently found to be devitrified. On the other hand, although old leaden roofs consist of metal showing coarse crystals, ancient iron shows practically the same structure as modern iron. We must remember that iron as a rule consists mainly of the crystalline phase, which is stable, not of the colloidal phase, which is metastable and can undergo slow hysteresis; besides, iron does not undergo annealing at ordinary temperatures.

Gold Ruby Glass.

The work of Zsigmondy, on gold ruby glass,[8] has given us an understanding of what happens when a metal is dispersed in glass. When gold is added to a glass melt (usually 1 part of gold chloride to from 3,000 to 10,000 glass), it dissolves, and the molten glass is colorless and upon slow cooling may become red or remain colorless, depending upon the nature of the batch. If quickly cooled to a set, all grades of gold ruby glass remain colorless. Upon reheating colorless ruby glass to the softening point, a portion of the dissolved or molecularly dispersed gold separates out upon nuclei or crystallization centers already formed in the previously chilled mass, and the glass usually develops its normal red color. Spoiled batches, upon reheating, generally yield a blue or violet shade, but may yield an unsatisfactory red. Reproduced in Table I are the ultramicroscopic observations of Zsigmondy made upon good

Table I.

Hot End	Good Ruby Glass (Color Red Decreasing ↓)	Spoiled Ruby Glass (Color Decreases ↓)
a, b	Color intense red. Numerous green ultramicrons, very close together, their brightness diminishing. ↓	Color blue. Ultramicrons fewer, copper-red, further apart.
b′	Homogeneous green light cone.	Color violet. Ultramicrons yellow.
c		Color bright red. Ultramicrons green.
d	Colorless and homogeneous.	Colorless. Few faint specks visible.
Cold End		

and upon spoiled ruby glass, using bright sunlight and a homogeneous immersion objective. Both specimens had been slowly cooled and then reheated more quickly than they had previously been chilled; they were heated so that at one end they began to melt (hot end), whereas at the other end they remained cold (cold end).

That with these particular specimens no new crystallization nuclei were formed upon reheating is evident from the fact that the average distance between the ultramicrons was the same in the intensely heated portions as in the less heated portions of the glass. "Colorless, slowly cooled gold ruby glass contains one part of its gold, therefore, in supersaturated solution, and the remainder in the form of nuclei so small that they affect the homogeneity of the glass only slightly or not at all. With batches of different composition, the temperature for the spontaneous formation of nuclei is so much higher that such glass colors up red on slow cooling."

* J. W. Grieg [*Am. J. Sci.*, 13, 1-44, 133-153 (1927)] found analogous phenomena on investigating immiscibility in silicate melts. Prof J. F. Ponomareff (Tomsk, Siberia), in a paper presented at Society of Glass Technology in Manchester, Eng., Jan. 1927 (see *J. Soc. Chem. Ind.*, 1927, 46, 170), reported that owing to the extremely slow speed of formation of spontaneous crystallization nuclei, with acid borates of sodium in mixtures approaching pure B_2O_3 it was necessary to maintain the optimum nuclei-forming temperature continuously for three weeks before crystals began to form.

Applying these principles to technical practice, Zsigmondy was able to explain certain heretofore incomprehensible observations. Thus, "The rim of a piece of pressed ruby glass remained colorless, while the middle became red. In the press the rim was more quickly cooled than the middle, and by subsequent heating was heated more quickly and to a higher temperature. Invesigation showed that the rim contained a much lesser number but considerably larger green gold particles than the rest of the glass. The rim of the glass had very quickly passed through the optimum temperature for the formation of nuclei, so that only few were formed; subsequent heating to a higher temperature, therefore, led to a speedy growth of these nuclei into particles of 110 to 145 mμ. The middle section of the glass had time enough to form a large number of nuclei, which, being less strongly heated, grew more slowly. In spoiled ruby glass the formation as well as the growth of nuclei is disturbed; fewer nuclei are formed and these grow more slowly than in good ruby glass."

DEVITRIFICATION OF GLASS.

Zsigmondy emphasizes the fact that the coloring of ruby glass should not be confounded with ordinary devitrification. "The difference between the two is that in the formation of ruby glass several milliards of nuclei exist and grow in a cubic millimeter, and that the hypothetical little crystals, of whose form and structure we know nothing, are so small that their presence changes only the visible appearance and not the working properties of the glass; whereas, in the case of devitrification, relatively few nuclei are present and lead to the formation of quite large crystals, which prevent the usual working up of the glass."

This difference is clearly seen on considering the facts brought out by N. L. Bowen in a valuable paper [9] on the devitrification of glass. While many silicates may be cooled quite slowly without crystallizing, $MgSiO_3$, Al_2SiO_5 and $CaSiO_3$ crystallize unless quickly chilled, a condition difficult of realization because molten silicates combine high thermal capacity with low thermal conductivity. The composition of the batch must be chosen to prevent supersaturation with any component at any temperature at which the glass is to be subsequently maintained. If devitrification occurs when the glass is cooled preparatory to working (or prior to the final stirring in the case of optical glass), the crystals formed are usually large. When the glass is cooled from the plastic to the rigid state, as during blowing, drawing, casting and particularly when optical glass is being cooled in the melting pots, devitrification may occur through the separation of spherulites or minute crystals uniformly disseminated throughout the glass, making it opalescent. Microscopically these crystals were found to be trydymite and cristobalite in most cases investigated. Particularly interesting is the fact that their formation is facilitated by "mineralizers" such as SO_3 or Cl; arsenic acts similarly if in excess, and fluorine may do so. This reminds one of a "salting out" action; the opposite or protective action of constituents in a melt is illustrated by the facts brought out in a paper [10] by H. F. Bellamy on gold ruby glass. His results show that SnO_2 acts as a powerful protector or stabilizer, deepening the color of the glass to such an extent when added in optimum proportions that the percentage of gold present has to be diminished.

The tin also keeps the color uniform over a range of reheating temperatures and prevents the development of light blue, purple or rose colors (which are indicative of coagulation or undue aggregation).

We have here a typical instance of protection in the colloidal sense, which

is quite in line with the work of Zsigmondy,[11] who showed that the purple of Cassius (an ammonia-soluble deep red precipitate obtained by mixing solutions of chloride of gold and stannous chloride) is simply colloidal gold stabilized by colloidal stannic acid. Berzelius regarded the purple of Cassius as a chemical combination of tin sesquioxide and purplish oxide of gold, and Gay-Lussac, Debray, Müller and others contributed to the extensive literature concerning it. Zsigmondy settled the moot question, for he actually synthesized the purple of Cassius by mixing together the hydrosols of gold and stannic acid, thus proving it to be an adsorption compound of the two.

A. Huber [12] examined the purple of Cassius with the X-ray spectrometer and confirmed the fact that none of the gold is in chemical combination.

G. S. Parks, H. M. Huffman and F. R. Cattoir (*J. Phys. Chem.*, **32**, 1366 (1928)) describe a glass made from pure anhydrous *d*-glucose, which slowly crystallized at room temperature, crystallization appearing to start always at some interface rather than within the glass. They suggest that the glass is "a colloid very much analogous to a jelly," rather than "a fourth state of matter" as suggested in their earlier paper (*J. Phys. Chem.*, **31**, 1842 (1927)).

Since glass and gelatin both exhibit "strain-figures" under polarized light, we may suspect that pressure produces a partial orientation analogous to that demonstrated in stretched or strained rubber by X-rays, which we may term *peizotropism.* In a similar manner, aged vanadium pentoxide sols show an orientation of their elongated particles in the direction of the flow of the liquid in which they are suspended, which might be justly termed *rheotropism.* These facts recall the mesomorphic states dealt with by G. Friedel in Vol I of this series. In view of the demonstrated molecular aggregations in glasses, it is certainly doing violence to the accepted meaning of the word "liquid" to speak of glasses as "solidified liquids," although there are many who perpetuate this error, now rendered obvious.

Crystallization.

Before considering the effects of the mechanical and heat treatment of metals and mixtures of metals (alloys), let us first try to follow mentally what happens upon the slow cooling of a hot saturated solution of a crystalloid salt —sodium chloride, for example, since it has no water of crystallization. As the kinetic energy of the system drops and the capacity of the water to maintain the salt molecules (or their ions) in motion diminishes, some salt molecules are extruded as it were from the solution, only to be dissolved again while others are extruded; for there exists a condition, not of static but of kinetic equilibrium, varying with the temperature.

Crystallization of Salt Solutions.

If, however, a number of salt molecules are extruded in such a position and so close to one another that they may cohere—i.e., within the radius of molecular attraction—they may form a crystal nucleus, or "crystallogen," which in proportion to its size will tend to take from the cooling solution more extruded molecules than it gives back. Such dominant nuclei tend to form on the relatively cooler walls of the containing vessel or on any added nucleus or foreign surface providing a "rear guard." Quick cooling produces more extruded molecules per unit of time, and agitation tends to bring the extruded molecules into contact; therefore both these factors tend toward the formation of more numerous and smaller crystals. Where large crystals are desired,

it is the practice in chemical works to crystallize in large tanks, which are carefully insulated and left undisturbed for weeks.

Extreme care is necessary to grow large perfect crystals from solution, the temperature being controlled within very narrow limits to maintain the slight degree of supersaturation at which no new nuclei or spontaneous crystals will form and yet the seed crystals (or large added nuclei) will grow. R. W. Moore [18] has grown clear, perfectly developed crystals of Rochelle salt 3 in. long, the process taking about a month in a thermostat sensitive to about 0.01 deg. C. Of particular interest is his statement that crystals grow faster near the bottom of the crystallizing vessel than at the top, for this is evidence of a gravitational accumulation of molecular groups (nuclei or "crystallogens") at the bottom quite analogous to the separation of the particles in colloidal solutions, as demonstrated by Perrin.

Crystallization continues until there is reached the kinetic equilibrium corresponding to the final temperature; and we have discrete crystals of sodium chloride bathed in a mother liquor containing a residual amount of salt in solution or true crystalloid dispersion. Impurities tend to collect in the mother liquor, and if they are protectors (in the colloidal sense) may inhibit or modify crystallization as they accumulate, as is the case with molasses, for example.

Crystallization of Pure Metal.

Even with pure metals under the best conditions, the path of crystallization is not as smooth as is the case with salt solutions, but is beset with complicating factors. There is no foreign restraining solvent, the viscosity is great, the attraction between the closely packed metal molecules is tremendous, and the metal soon forms a hard skin so that the interior crystals are formed under pressure or strain. With some metals there may be formed a geode-like center, where slower cooling, freedom from crystal-inhibiting substance, and lessened or more equalized strain may result in the formation of large well-developed crystals.

But the metal seldom reaches the crystallization equilibrium, toward which it strives, for the enormous increase in viscosity which accompanies its rapid loss of heat prevents the aggregation tendencies of the metal molecules from entirely establishing themselves, and there results a mass of metallic crystals embedded in a finely dispersed solid metallic "mother liquor," the so-called amorphous phase.

The amorphous phase is colloidal, as its name, appearance and properties indicate, and contains a mixture of submicroscopic crystals or crystal fragments with unoriented or random clusters, possibly in the form of isotropic globulites; for the globulitic form, according to many investigators, seems to be a precursor of the crystalline condition. At higher temperatures the whole metal probably exists as an isocolloid. The extent to which this state is altered in the direction of a visibly crystalline mass, embedded in a colloidal matrix, depends largely upon the speed of chilling. In impure metals and in alloys the composition of the phases and the presence of substances which hasten or inhibit crystallization are important factors.

Von Weimarn held the view, in which the writer does not concur, that all molecules and molecular groups are crystalline, that crystallinity is the only internal state of matter and that in general no amorphous substances exist in nature. This view would give to the words "amorphous" and "crystalline" significations they do not at present possess. Besides the X-ray spectroscope shows [14] that many organic colloids, such as gelatin and starch, and also some

inorganic colloids (silicic acid and stannic hydrosols) consist of or contain groups of molecules arranged in an unoriented, haphazard or random manner; so that even if the molecules themselves are crystal prototypes, they can and do occur in non-crystalline groups.

Zay Jeffries [15] has shown that with metals, in general, the cohesion of the amorphous phase equals that of the crystalline phase at the lowest recrystallization temperature, which he terms, therefore, the equicohesive temperature; and based on this he has explained the mechanical behavior of metals at various temperatures. At higher temperatures than the equicohesive point, the cohesion of the amorphous phase decreases more rapidly than that of the crystalline phase—i.e., it becomes relatively softer—whereas at lower temperatures than the equicohesive point its cohesion is greater and increases with much greater

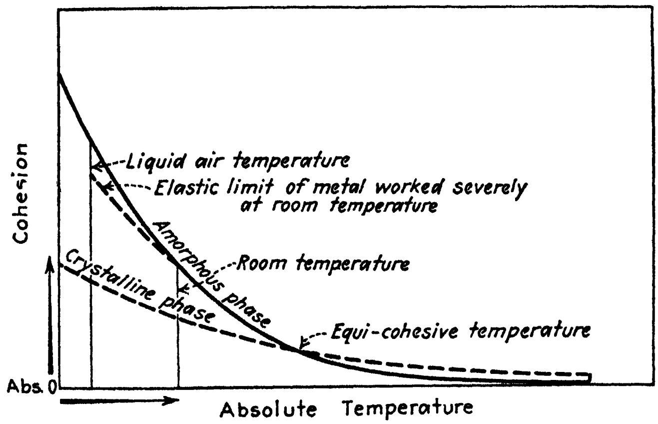

FIG. 1.

rapidity than that of the crystalline phase. Fig. 1, taken from Jeffries' paper, shows these facts diagrammatically.*

These differences between the two phases are intelligible from the following considerations: The atoms in the crystalline phase, though arranged in regular layers, are on the average closer packed,[16] and therefore at lower temperatures cannot draw together as much as those of the amorphous phase, which consequently becomes relatively stronger at lower temperatures; whereas at higher temperatures, the molecules of the amorphous phase become separated and mobile more readily than those of the crystalline phase, for they possess initially more potential energy [17] since they are less closely packed—i.e., further apart on the average—and are, therefore, less strongly held to one another by molecular forces; consequently the amorphous phase becomes relatively weaker at higher temperatures.

RECRYSTALLIZATION.

As a result of this preferential softening, the amorphous or colloidal phase, at relatively higher temperatures, acts like a very viscous solvent surrounding and nourishing the more rigid crystals; and as increasing temperature renders this solvent less viscous, the metal strives toward crystallinity, which represents the position of minimum mechanical potential. Some metals, like lead,

* It would be interesting to test the relation between the equicohesive temperature and the zone of maximum colloidality. See the first paper in Vol. I of this series, especially the results of Sauveur.

undergo such molecular readjustment, even at room temperatures. During this process of recrystallization below the melting point it has been observed that, in general, large crystals tend to grow at the expense of the small ones. A similar process is observable in the crystallization of salts, for, as Hulett has shown, finely ground powders are more soluble than a coarse grinding of the same substance. Therefore, the smaller metal crystals would preferentially dissolve in the "amorphous" or colloidal phase. Bearing in mind that the growth of a crystal means that there are deposited upon it more molecules or molecular groups (crystallogens) than are dissolved off, the larger masses would naturally get most of these extruded units, just as happens in the cosmic field.* The larger crystals have the advantage of exposing to the solvent action of the amorphous or colloidal phase less surface per unit of mass; and when metal molecules or molecular groups deposit on a crystal, they release a certain amount of energy, the heat of crystallization or latent heat of fusion, which helps to make the amorphous or colloidal phase more fluid.

Do the small crystals dissolve molecule by molecule, or in molecular masses or groups as well? It would seem that in some cases at least molecular groups are dissolved off and transported, for in strained metals especially recrystallization is extremely rapid. Thus in sheet aluminum,[18] when heated to a suitable temperature, recrystallization takes place like a flash, the originally smooth sheet becoming coarsely granular, suddenly, before one's eyes. The writer has observed [19] ultramicroscopic particles streaming from a crystal of sodium citrate as it went into solution, indicating that initially solution took place, at least partially, in colloidal molecular masses.

The amorphous or colloidal phase becomes, therefore, a medium for the transfer of atoms, molecules or molecular groups from the small to the larger crystals, and also tends to annihilate itself by allowing its constituent oriented and unoriented particles to be incorporated into the huge Juggernaut crystals.

The preceding remarks have been based upon a consideration of *pure* metals, which are practically never met with, for most commercially pure metals contain as impurities several other metals, elements or compounds. Besides, most metals are used in the form of mixtures or alloys—steel, brass, bronze, type-metal, babbitt metal, solder, etc. The introduction into a metal of a single impurity, even in minute percentage, usually produces a very marked change in its properties or behavior—for example, 1 part of carbon in 10,000 of iron, or 1 part of copper in 10,000 of gold—and as it seems to me that in many cases this effect involves, at some stage, the direction, modification or inhibition of the normal crystallization of the metal by a colloidal dispersion of some substance or substances, it is desirable at this point to consider the general question of the effect of colloids upon crystallization.

Most experiments in this field have been made with aqueous solutions or dispersions, and the rule seems to be that a colloid which is adsorbed by, or which forms an adsorption compound with, the initial colloidal aggregations of the crystallizing substances either prevents the growth of its crystals or groups beyond colloidal dimensions or else forces their growth to assume globulitic or dendritic forms which vary with each substance, each colloid and each set of conditions. Thus gelatin, gum arabic and similar stabilizing or protective colloids, even in small quantity, oppose the aggregation of the gold atoms at the instant of their liberation to such an extent as to yield a highly dispersed hydrosol under conditions that would otherwise yield a coarse blue or black gold suspension. The use of gelatin (about ½ per cent), eggs and similar colloids in ice cream [20] leads to the production and stabiliza-

* *See* paper by MacMillan in Vol. I of this series.

tion of very fine or colloidal ice particles, giving the product the desired smooth velvety texture; without colloids the ice cream becomes grainy or sandy, the undesirable roughness being due to large or spicular crystals.

Coming now to substances which form solid crystals at ordinary temperatures, we see that colloids exert a powerful inhibitory action on the crystallization of plaster of paris,[21] not only preventing the formation of ordinary crystals but delaying or even entirely preventing the "setting."

The effect of colloids on the crystallization of ordinary salts is most remarkable.[22] With each salt, each colloid and each set of conditions (concentration, temperature and pressure) there are formed characteristic groupings in which dendrites and spherulites are exceedingly common; also very beautiful and complicated leaf-like, branching and cellular forms, reminding one forcibly of living structures.* Indeed it seems evident that the growth and shape of living organisms are largely controlled by the complex interplay of the forces of crystalline growth, as restrained, modified and directed by colloidal substances.

If the amount of colloid is so small that it is all adsorbed by these structures before the salt has entirely crystallized, well-defined crystals of the colloid-free salt may appear. On the other hand, if enough of the colloid is present, ordinary visible crystallization may be entirely prevented; and in intermediate cases abortive attempts at crystallization register themselves in curious formations. The preparation of a few microscopic slides with solutions of NaCl, $MgSO_4$, Na_2SO_4 and Na_2CO_3, containing from 0.5 to 50 per cent (figured on the dry salt) of gum arabic or gelatin, will give some idea of these effects [23] and show their striking resemblance to the microstructure of metals. The slides may be made by putting on a drop of the mixture and allowing it to dry without a cover glass. During the drying, changes in temperature and concentration occur within the drop, with the result that the field changes progressively from the center.

Production of Fine Grain.

This resemblance led me to comment [24] as follows regarding metals:

"Since coarsely crystalline metals are brittle, tending to split along the lines of crystal cleavage, various physical and chemical means are employed in technical practice to obtain a hard, fine-grained structure.[25] Among the physical methods are chilling and rolling, while the chemical methods involve the removal of undesirable constituents (as in the conversion of pig iron into steel), or the addition of desirable constituents (as in case-hardening and the manufacturing of 'chromium steel' and 'nickel steel'). For example, P. Pütz [26] has shown that the predominant effect of vanadium in steel is to decrease the size of the ferrite grains and make the material harder; it renders the ordinary structure due to pearlite fine-grained and homogeneous.[27]

"Now while the question is one of very great complexity, many of the facts at present available seem to indicate that one of the causes favoring the fine-grained structure is the inhibition of crystallization by substances colloidally dissolved in the molten mass. Thus, part of the carbon in iron and steel exists in the graphitic form, and as graphite is slightly soluble in iron [28] some of it will, under proper conditions, be found in colloidal form.[29] Besides, metals may dissolve one another and other substances colloidally, but in the case of ordinary metals this is not easy to demonstrate, although a differential solvent acting in the presence of a protective colloid might leave a colloidal residue."

Amorphous Metal and Cold Work.

In conclusion let us consider some of the aspects of the amorphous theory regarding the change of metals under strain, which is stated by one of its principal advocates, Rosenhain, as follows: [30]

* See papers by Leduc, Herrera, and Alexander and Bridges in Vol. II of this series.

"It may be well to state precisely what is understood, in this connection, by the term 'amorphous.' In accordance with Beilby's views and their recent development by the author [Rosenhain] and his collaborators,[31] the amorphous condition is one in which the crystalline arrangement of the molecules is completely broken up, so that the molecules remain in a state of irregular arrangement similar to that which is supposed to exist in the liquid state. In fact, the amorphous phase is regarded as being—from the point of view of the phase doctrine—identical with the liquid phase. Now extremely undercooled liquids are well known in such substances as glass, vitreous silica, etc., and they are hard, brittle bodies devoid of placticity and of crystalline structure. Amorphous metal is, therefore, to be regarded as being identical in nature with the liquid metal if that could be cooled down to the ordinary temperature without undergoing crystallization. It is admitted that such extreme undercooling of metals has never been actually accomplished, and objections to the whole concept of amorphous metal have been based on that ground. These cannot be dicussed here, but they have been fully dealt with by the author [Rosenhain] elsewhere.[32] At the present moment it may well be claimed that the theory of an amorphous phase in metals, produced as a result of mechanical disruption of the crystalline arrangement of the molecules, holds the field as the best working hypothesis available. There are admittedly outstanding difficulties, but these the author regards as being inevitable in a theory whose wide generalizations cover a field which has as yet been but partially explored.[33]

Effect of Plastic Deformation.

"The general effect of slowly applied or 'static' plastic deformation may be summarized as follows: The metal in the cast or the annealed state is an aggregate of crystals; when the metal undergoes plastic deformation, the crystals are deformed in the same general sense as the mass of metal. This change of shape of the crystals is accomplished by a process of slip or gliding by which layers of the crystal slide over one another along certain gliding planes. Such slip occurs on a great multitude of planes in each direction and, as a rule, it must occur on at least three sets of planes, but it may occur on a greater number. This slip is accompanied by a certain disturbance of the crystalline arrangement of the molecules on or near the surfaces of the slip. If the deformation has been slight, the disturbed molecules may be able to rearrange themselves in accordance with the crystalline system by which they are surrounded, and the completely crystalline character of the metal will then be unaffected by the deformation. When the deformation is severe and if it is intensely localized, as when a single crystal is bent upon itself, the molecular disturbances at the slip surfaces become larger and permanent layers of amorphous metal are formed on each surface where slip has occurred. Ultimately the metal, as a result of extreme deformation, becomes a mass of crystal fragments embedded in relatively thick layers of amorphous material. This change is accompanied by an increase in the hardness of the metal and—in the majority of metals—by a measurable decrease in density."

This amorphous view stresses particularly the entire absence of regular orientation or crystallization in the so-called amorphous phase, whose molecules are supposed to be in the random and, mainly, isolated state assumed to exist in liquids. I believe, however, that the amorphous phase consists largely, if not entirely, of molecular groups, many of which may be oriented in the form of ultramicroscopic crystals or crystal fragments; and that its properties are due, not to the entire lack of orientation among its particles, but rather to the fact that many or the majority of its molecular groups are of colloidal dimensions. Since in metals the molecules are very close together and possess extremely high cohesion or crystallization tendency, it does not seem possible that the amorphous phase can be composed entirely of isolated molecules, or even entirely of non-crystalline groups. With gold hydrosols where the dispersing water exercises a restraining influence, the X-ray spectroscope shows that the ultramicroscopic, and even that the amicroscopic, gold particles are crystalline. With the most drastically chilled metal, allowing for the high viscosity and its rapid increase, it does not appear conceivable that no tiny ultramicroscopic crystals form, or at least that there is no grouping, regular or irregular, of the metal molecules. The facts indicate and are in harmony

with the conception of amorphous metal as an isocolloid—that is, as a dispersion of colloid crystals, crystal fragments or non-crystalline groups in still more finely dispersed metal—or else a mixture of colloidal crystalline and non-crystalline groups, forming a solid gel-like mass. The fineness of its particles and the enormous development of free surface found in all colloids are its critical factors.

The idea here advanced, that metals, in the course of their aggregation, pass through a colloidal stage which exerts a powerful influence on their structure and properties and may even be partly retained in the final product by "protection," adsorption, crystallization or increase in viscosity due to quenching, is not limited to the field of metallurgy, but may be applied to any substance or system where a portion or a component becomes colloidal while the remaining portion or components are outside of the colloidal zone.

Influence of Atomic Groups.

Liquids appear to consist largely of atomic or molecular groups and solids of still more complex groups, the size and nature of which depend upon conditions;[34] and among these groups those of colloidal dimensions as a rule appear and must then be reckoned with. The "twinning" of crystals,[35] which is a marked characteristic of γ iron, α brass, and especially of worked or strained metals on annealing, is probably due to colloidal influences.

This and many other questions, such as the effect of other metals on iron and steel (so-called alloy steels) and the adsorption of gases at the free metallic interfaces, etc., though germane to this paper, must be left for future consideration. The work of P. W. Bridgman[36] with high pressure is very suggestive. For example, he found that, whereas cylinders of soft tool steel (1.25 per cent C) and soft chromium-nickel steel (Krupp Special E.C. 60.0) ruptured under the same pressures, whether water or mercury was the pressure-carrying fluid in contact with the metal, the same steels when hardened broke at much lower pressures (about one-third) with mercury than with water. The rupture was due to the amalgamation of the steel, which when once started spreads rapidly under the high hydrostatic pressure.*

But even a pressure of 6,500 atmospheres for 12 hours failed to cause the amalgamation of hard or soft steel rods, although the rods were polished with fine emery paper immediately before being plunged into the mercury. On the other hand, hard and soft steels and cast iron (also Al, Ni and Co) were promptly amalgamated on the fresh surfaces formed by breaking the metals under mercury.

Bridgman speaks of "dirt" preventing amalgamation; but from the recent work of W. B. Hardy, on fresh surfaces, and of I. Langmuir and others, on adsorption, it would seem that instantaneous adsorption from the atmosphere, probably of gases, is responsible, although a change in the nature of the surface may have some effect also. Freshly cleaved sheets of mica show a similar effect; their initial coherence is speedily lost. With steel, as with gelatin jellies, the quickly chilled specimens show greater porosity because of the greater total area of the diffusion paths consequent upon finer subdivision.

Iron and Steel.†

The enormous literature that exists regarding the iron-carbon alloys exhibits at once their great importance and exceeding complexity, and within

* On the effects of tiny cracks in the structure of metals, irregularities in crystals, etc., *see* paper by McBain and Alexander in this volume.

† A discussion of some other alloy system is given in J. Alexander, "Colloid Chemistry," 3rd ed., 1929; also in *Chem. and Met. Eng.* (1922).

the brief limits of this paper only a few of the most striking facts can be dealt with. Since the behavior of the iron-carbon alloys is greatly influenced by the allotropic changes of iron itself, it will perhaps be best, first, to consider what these are, according to the evidence available.

Allotropy of Iron.

After freezing at about 1,505 deg. C., pure iron, upon further cooling, shows a large evolution of heat at about 900 deg., known as the thermal arrest point Ar_3, and a smaller evolution of heat at about 780 deg., known as the thermal arrest point Ar_2. It is generally accepted as a fact that above 900 deg. the iron exists in the γ form, which is non-magnetic, and below 780 deg. in another allotropic α form, which is magnetic and exhibits a different crystallization from γ iron. Rosenhain believed [37] that the weight of evidence shows that between 900 and 780 deg. the iron exists in a third allotropic form, known as β iron, which has the same crystal form as α iron, but resembles γ iron in being non-magnetic. Benedicks,[38] on the other hand, believed that the evolution of heat at 780 deg. indicates, not a transformation of a β allotrope into α iron, but the final disappearance of persistent γ iron molecules from the metal.

Considering the recent work on the allotropism of sulfur, it seems that these apparently conflicting views can be reconciled by regarding the iron between these temperatures (900 and 780 deg.) as an allocolloid or allodispersoid, the so-called "β iron" being an α-γ adsorption compound (α iron dispersed in γ iron), whose break-up into the more completely oriented α iron sets free the relatively smaller amount of heat at the point Ar_2. This view accounts for the following facts: (1) that "β iron" has the same crystal form as its "dominant partner," α iron, but, unlike it, is not magnetic—for magnetism seems to depend upon a peculiar regular molecular orientation; [39] (2) that γ iron dissolves iron carbide, whereas "β iron" and α iron do not; for whatever γ iron exists in the β zone is adsorbed by or in some kind of loose combination with the dominant α iron and is not free to exert its solvent power on iron carbide; (3) that an increase in strength is noted when α iron is transformed into "β iron"; for the formation of some γ iron by increase of temperature over about 780 deg. results in the formation of the α-γ adsorption compound, which increases the free surface and strength of the system; (4) that the structure of "β iron" is finely acicular, indicative of crystallization in the presence of a colloid.

Does Austenite Contain Molecular Carbon or Cementite?

Leaving this moot question, however, let us consider the behavior as noted in the equilibrium diagram of a low-carbon steel, containing, say, 0.2 per cent of carbon, which dissolves in the liquid iron as Fe_3C. From freezing down to 840 deg. this steel consists of an apparently homogeneous "solid solution" or dispersion of iron carbide or cementite in γ iron.

In a paper [40] entitled "The Slip Interference Theory of the Hardening of Metals," Jeffries and Archer state:

"There is good reason to believe, however, that in all cases solid solutions are characterized by the *atomic* dispersion of their components." This is true only if the expression "solid solution" is limited to such dispersions; but most solid solutions contain aggregates, just as do many or even most ordinary solutions, especially if concentrated. Jeffries and Archer further state that "the carbon in austenite is present as individual atoms of carbon"; that "these atoms are undoubtedly held strongly to the neighboring iron atoms, but

the union is not permanent. Diffusion must consist in a migration of carbon atoms and not of groups or 'molecules' containing several iron atoms. Such groups could not, on account of their size, diffuse through solid iron."

It seems to the present writer that there is no good reason to doubt the existence of Fe_3C, especially when the steel is semi-solid or solid. For there exists a condition of kinetic or dynamic equilibrium in which this compound is being continually formed and broken up, so that while a certain per cent of free carbon atoms may exist at any one moment, there is probably an enormously larger percentage of Fe_3C. Viewed from the standpoint of a kinetic equilibrium, all difficulty regarding the diffusion of Fe_3C disappear.[41]

With large amounts of carbon, as in cast irons, much of the C is thrown out on cooling and forms graphite, or under conditions of quick cooling or high pressure may form diamonds, as Moissan has shown.

At any rate, at 840 deg. C. (Ar_3), the "solid solution" transforms into a α-γ dispersion ("β iron"), and at 750 deg. C. (Ar_2), the residual α-γ adsorption compound decomposes into α iron, the steel now consisting of α iron crystals dispersed in a "solid solution" of iron carbide in γ iron. With further cooling, the quantity of α iron crystals increases, until at a little below 700 deg. C. (Ar_1), the remaining γ iron-carbide solid solution is transformed into a eutectoid mixture of α iron (ferrite) and iron carbide (cementite), with an evolution of heat.

Reactions at 690° C.

This last transformation seems to be the break-up of an adsorption compound between γ iron and iron carbide, the former transforming into α iron and the latter being set free to form aggregations of its own. This adsorption compound is the cause of the carrying over of some of the γ iron through the so-called "β iron" zone to the eutectoid point, where, with increasing carbon content, increasing quantities of heat are evolved, the allotropic transformation of the iron itself becoming practically negligible after the steel contains about 0.5 per cent carbon (equal to about 7.5 per cent Fe_3C). In fact, steel of "eutectoid composition" (about 0.9 per cent C, or about 13.5 per cent Fe_3C) exhibits only a single thermal arrest point, at which it glows visibly. This phenomenon is known as "recalescence"; it is indicative of a sudden large release of energy consequent upon the breakdown of the extensive metastable system built up of γ iron and cementite, two delayed transformations occurring simultaneously—the iron transforms from γ into α and at the same time the released cementite aggregates. The inhibition of the allotropic iron transformation shows that in eutectoid steel the large percentage of Fe_3C has carried over practically all the γ iron in metastable condition to the eutectoid point. The presence of such elements as silicon and manganese will perceptibly change the location of the eutectoid point, a fact which fits in with the easy disturbance of colloidal systems by foreign substances or "impurities."[42]

But whether this view is accepted or whether the change is regarded as a separation of carbide from "γ iron solid solution," one thing is certain—there is suddenly released from some kind of solution or combination Fe_3C, an insoluble substance possessing considerable cohesion, which promptly causes it to attempt to aggregate against the interference offered by the now highly viscous iron. This is an ideal condition for the development of a colloidal system; but the cohesive power of the cementite is so great that in unquenched steel it usually appears interspersed with α iron, or ferrite, as fine plates or fibrils, yielding the finely laminated structure known as "pearlite" because

under proper illumination it exhibits the iridescent luster of mother of pearl. This iridescence, reminding one of that of a diffraction grating, is evidence of the fineness of the pearlitic structure, which, like Pleurosigma, taxes the highest powers of the microscope for its successful resolution, the lamellæ being often less than 0.2 μ apart.

Divorce of Cementite.

As shown microscopically, e.g., by Rawdon, eutectoid steel (approximately 0.9 per cent of C) when slowly cooled consists entirely of pearlite, thus corresponding to the pure eutectic of ordinary alloys.[48] But with very slowly cooled steel, or with steel reheated for a long time at about 900 deg., the cementite tends to group up still further into balls or globules, the liberated ferrite forming larger crystals at the same time.

"The cementite when present as isolated balls or lumps is of very little use to the steel, which then possesses merely the properties of pure ferrite having a coarse structure—these, of course, being far from equal to those of a mild steel having the correct structure. . . . When in the condition of pearlite or sorbite, where cementite is intimately associated with layers of ductile ferrite, the inherent brittleness of cementite is largely neutralized, and the hardness of the duplex constituent—pearlite—is well adjusted to stiffen and support the ferrite matrix of a mild steel. Cementite of itself, however, is not only excessively hard and brittle, as compared with ferrite, but it is also too small in quantity and bulk to serve as an efficient stiffener. Its presence in the isolated state thus becomes a source of weakness rather than strength. The behavior, both under test and in service, of steels having this 'free cementite' structure is now well recognized as most unsatisfactory." (Rosenhain, p. 278.)

Quenched or quickly cooled steels, on the other hand, exhibit an entirely different set of microscopic pictures and mechanical properties from slowly cooled steel, which vary with the speed of chilling. Arranged in order of their formation on progressive cooling, the following constituent forms of the iron-iron carbide dispersion are recognized by metallurgists:

Nature of Structures in Hardened Steel.

Austenite.—White, apparently structureless γ iron solid solution, when preserved as such down to ordinary temperatures, either as the result of quenching or by the presence of a third alloying element inhibiting its decomposition—i.e., manganese in manganese steels.

Martensite.—The first stage in the aggregation of the γ iron solid solution; the hardest constituent of hardened steels; it varies widely in the details of its structure, but is mainly acicular.

"When steel has been quenched from very high temperatures,[44] the martensite is found to occur in large grains showing a rather coarse acicular structure. When, on the other hand, a steel of eutectoid composition is quenched at a temperature just above the critical point Ar_1, then the structure of the resulting martensite is exceedingly fine—so fine, indeed, that some workers, not perhaps provided with the best of microscopic appliances or employing unsatisfactory etching methods, have failed to detect the acicular structure, and have claimed that the best hardened steel contains a structureless 'martensite,' which they have sometimes distinguished by the term 'hardenite'—a purely local term whose general use is not to be recommended. The careful examination of samples of the best and most carefully hardened steels, however, has convinced both the author [Rosenhain] and the majority of impartial observers that martensite can always be shown to have an acicular structure, although in 'properly hardened' steel that structure is exceedingly minute." (Rosenhain, p. 179.)

Troostite.—A dark-etching constituent with characteristic rounded or woolly outlines, found particularly in hypoeutectoid steels at the edges of

martensite grains, especially where they border on ferrite. By a suitable rate of cooling, or by proper tempering, martensite can be entirely converted into troostite.

"It is sufficient for our present purpose to regard troostite as a further step in the degradation of austenite into ferrite plus pearlite. The dark color appears to be due to the condition of the carbon in this stage; the separation of the dissolved carbide from the iron must have begun as soon as the first particles of γ iron became transformed into the β or α condition. In the martensite stage the separation makes itself felt only very slightly by the small difference of color between the various systems of interlacing needles. When the troostite stage is reached we are probably dealing with a material in which the separated iron carbide is present in slightly larger masses. According to Benedicks,[45] the carbide in troostite is present as a colloidal suspension,[46] * and it is quite probable that troostite differs from martensite only by the slightly greater segregation of the carbide particles." (Rosenhain, p. 183.)

In the paper by Benedicks cited by Rosenhain, the Swedish scientist remarks:

"After studying some of the colloid literature, it was entirely clear to me as far back as 1905 that the nature of troostite is simply explained; it is a *solid colloidal "solution" of cementite in iron* (*a solid cementite ferrosol*). In other words, troostite may be conceived of as a highly dispersed intermediate between martensite, the true solid solution, and pearlite, the coagulum. . . . Troostite is a pearlite in which the constituent particles are ultramicroscopically small."

With steel containing 1 per cent carbon, Benedicks obtained the following results, the test-pieces being cylinders 50 mm. long $\times$ 6.5 mm. in diameter:

Temperature, of Steel, Deg. C.	Time of Cooling to 100 Deg. C. Seconds	Result of Microscopic Examination
950	3.07	Only martensite
848	4.32	Only martensite
750	4.11	Only martensite
715	5.33	Martensite with traces of troostite
695	6.2	Martensite with traces of troostite
725	9.5	All troostite

The last specimen had been wound with 1 mm. iron wire so that its weight was increased from 12.3 to 27.5 g., thus lengthening the cooling period. From this it is evident that the speed of aggregation is so great that within a few seconds all the martensite may be transformed into troostite.

Sorbite.—

"When the rate of cooling is further lessened or the temperature of reheating or tempering is further increased, the steel is permitted to progress somewhat further toward the final state of ferrite plus cementite. Instead of the troostite described above, we find a constituent still devoid of any visible detailed structure under the highest available magnifications, but not etching to such a deep color as troostite and without the peculiar rounded outlines. This is often called 'sorbite,' but it may be regarded as simply a variety of pearlite in which the two constituents are so finely divided that they cannot be microscopically separated. The dividing line between pearlite and sorbite, indeed, is simply a question of microscopic resolving power." (Rosenhain, pp. 182, 184.)

Pearlite.—This microscopically resolvable dispersion of Fe_3C in ferrite has been previously dealt with.

Before discussing the facts above stated, it will be convenient to tabulate the main features:

* As will be seen later, in troostite the cementite particles have already grown almost or quite beyond the colloidal stage. In martensite, however, some of the carbide is so fine that the carbon released by the action of acid is reduced by the nascent hydrogen, forming a variety of hydrocarbons.

TABLE II. *Nature of Structures in Heat-Treated Steel.*

Iron-Cementite Dispersions	Nature of Dispersion	Crystal Structure
Austenite	"Solid solution"	Structureless streaks.
Hardenite	Colloidal	Structureless martensite.
Martensite	Colloidal	Generally acicular; varies, may be very fine.
Troostite	Coagulation begun	Rounded or woolly (globulitic).
Sorbite	Coagulum	Fine pearlite, not microscopically resolvable.
Pearlite	Coagulum	Laminated; may segregate into balls.

An illustration in Prof. H. C. H. Carpenter's paper on "The Hardening of Steel,"[47] shows graphically the changes in the thermal arrest points in steel with gradually increasing carbon content (Fig. 2).

Granting that in austenite the cementite is in true molecular dispersion, which appears very doubtful especially after solidification has begun, it seems

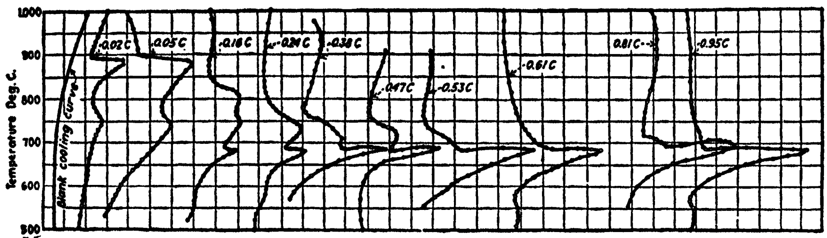

FIG. 2.—Changes in the thermal arrest points of steel with increasing carbon content.

evident that, of the remaining members of the iron-cementite dispersion systems, martensite and troostite are to be regarded as within or approaching the colloidal zone of dispersion, whereas sorbite and pearlite are coagula of the pre-existent colloidal systems, the latter visibly so. In the colloidal systems martensite and troostite, cementite (Fe_3C) is the dispersed phase and iron the dispersing phase; for this is shown by the nature of the pearlite coagulum, which consists of cementite interspersed in ferrite. In martensite, crystal formation is only incipient, inhibited by the high viscosity of the dispersing medium, and perhaps also by the adsorption of a small residual quantity of γ iron (consequent upon lag in its transformation), or of impurities. With troostite the globulitic stage is reached, often found in crystallization inhibited by colloids, and reminding one somewhat of the "clumping" of typhoid bacteria in the Widal test. It must be remembered that metal surfaces etched by various reagents are artifacts, from which the original detail of the unetched metal must be inferred.

VARIATIONS IN DISPERSIONS.

Although theoretically there is no sharp line of demarcation between any of the members of the iron-cementite dispersion series, the sorbite-pearlite group shows the characteristics of coagulated colloids or gels, as opposed to the martensite-troostite group which represents higher dispersion, with troostite already appreciably on the road to coagulation. With milk, upon great dilution, the gradual aggregation of the actively moving ultramicroscopic particles of the casein sol may be watched in detail over a period of half an hour or more.[48] The ultramicrons first form occasional groups of two ("diplococci") and then larger and more numerous groups, until finally the whole casein lies quiet on the slide in large grape-like masses of curd, which under dark field illumination show the reticulated structure characteristic of such gels, and

TABLE III. *Condition of Steel at Various Temperatures.*

Pure Iron	0.2 Per Cent Steel	0.9 Per Cent Steel
γ Iron	γ iron-cementite solid solution.	This is eutectoid steel. So much cementite is present that no α-γ adsorption compound is formed, the γ iron being held in metastable condition by the cementite, down to Ar_1.
900 deg. C. (Ar_3) γ iron forms α-γ adsorption compound (β iron). Largest thermal point.		
	840 deg. C. (Ar_3) α-γ compound (or β iron) forms late because of cementite.	
Allocolloidal Zone		
	750 deg. C. (Ar_2) α-γ compound (β iron) changes to α iron.	
780 deg. C. (Ar_2) α-γ compound (β iron) decomposes into α iron.		
	700 deg. C. (Ar_1) γ iron-cementite "adsorption" compound decomposes, γ iron changes to α iron, and cementite is liberated and aggregates.	700 deg. C. ($Ar_{3,2,1}$) Sudden change of all the iron from γ to α, with liberation of all the cementite.
α Iron.	α iron and cementite.	pearlite.

remind one forcibly of very fine martensite, which, however, usually registers the high crystallization tendency present in its constituents, but absent in casein. The positive inhibition of the coagulation of the casein by "protectors" (gelatin, gum arabic, sodium citrate) may also be visually demonstrated. With clays, too, similar differences in aggregation may be noticed,[49] especially "diplococci" and the reticulated structure. But with metals, owing to the dense concentration of their particles, the rapidity of the changes and the high temperatures at which they occur and the practical impossibility of obtaining transparent sections [50] without disturbing the *status quo*, it will probably be impossible to settle moot points with the ultramicroscope alone. Perhaps, as before indicated, the X-ray spectrometer * will aid, small pieces or drops of fluid metal being drastically quenched in liquid air or other liquid gas; or an ultramicroscopic examination of gold, silver or other metal leaf or mirrors, or of films of mercury or amalgams; or the solution of metal by a differential solvent, in the presence of a "protector."

* Jeffries and Archer, *Chem. Met. Eng.*, **24**, 1065 (1920), reported preliminary results with the X-ray spectrometer as follows:
(1) Non-magnetic steels show face-centered cubic lattices (γ iron).
(2) Magnetic steels show body-centered lattices (α iron).
"A 1.5 per cent C steel quenched from above the critical in iced brine showed both martensite and austenite under the microscope, and the X-ray spectrometer pattern showed both face- and body-centered lattices. A 0.35 per cent C steel quenched from above Ac_3 showed only martensite under the microscope and only a body-centered lattice with the X-ray spectrometer." These results confirm the views above expressed, and, as the authors state, they indicate that the transformation from austenite to martensite represents a substantially complete change from γ to α iron. They further show that quick chilling may save some of the iron in γ form. As Benedicks' work shows, the speed of transformation is very rapid, so that only by the drastic chilling of small specimens as above suggested will much of the γ iron be maintained. Interesting results can be obtained, no doubt, with low melting point metals like mercury, gallium, and with Wood's and Rose's alloys, by quick chilling in liquid air, CO_2 or N, being followed by X-ray examination while cold.

Hydrocarbons Formed on Dissolving Martensite.

Meanwhile there is other distinct evidence of the colloidal nature of the cementite in hardened steel. Prof. H. C. H. Carpenter, speaking first of annealed or slowly cooled steel, says: [47]

"This carbide can be separated from the steel by appropriate solvents which remove the iron. On the other hand, it is not possible to separate any carbide of iron from a properly quenched tool steel. When the latter is treated with dilute acids, the steel dissolves without residue and liberates a complicated mixture of hydrocarbons, both liquid and gaseous. There is, therefore, a fundamental difference in the form of the carbide in a quenched as compared with an annealed steel. In the former it is wholly dissolved, in the latter wholly segregated."

This last statement is too dogmatic, and Prof. Carpenter, evidently applying the adage quoted by Ramsay, *Natura nihil fit per saltum,* retrieves it by continuing:

"When hardened steel is softened by annealing, the carbide of iron is gradually precipitated. If the annealing be carried out at low temperatures it is precipitated in the form of ultramicroscopic particles which are known as troostite. On raising the temperature the troostite passes into another variety known as sorbite, and at still higher temperatures well-segregated pearlite results. The gradual tempering and softening of hardened steel is caused by the precipitation of iron carbide in these forms, together with the soft α iron, and as to this no difference of opinion exists."

The formation of hydrocarbons upon the solution of hardened steel in acid shows that the particles of Fe_3C are so small that upon their decomposition the nascent hydrogen is able to combine with the liberated carbon, which must appear in particles approximating molecular dimensions and within the range of molecular attraction. The variety of hydrocarbons formed is evidence of the great diversity in the size of the carbide groups rather than of the existence of a number of different carbides, or "chemical compounds"—in other words, the carbide in properly hardened tool steel exists almost entirely in colloidal form. Great chemical activity is generally consequent upon colloidal dispersion—thus Raffo and Pierni showed that, while fine precipitated sulfur does not affect silver salts in the cold, and does so only partly upon boiling, colloidal sulfur reduces them energetically even at ordinary temperatures. Fine lead, produced by heating dry lead tartrate in a tube, takes fire instantly in the air, as does the phosphorus left upon the evaporation of the solvent CS_2 or ether.

Waiving the question as to whether the cementite in austenite is colloidal (and I think that at least as the steel freezes it becomes so), it seems that the very hard martensite is a colloidal dispersion of cementite in iron, a cementite ferrosol, with "hardenite" as its higher dispersion, troostite its incipient globulitic aggregation product, and sorbite and pearlite its successive coagulation stages. This view will perhaps reconcile the "allotropic" and "amorphous" theories which have been advanced to answer the question as to the constitution of martensite and the cause of its great hardness. According to the former:

The hardness of martensite is due to the presence in it of a notable proportion of "hard" β iron . . . the acicular structure of martensite would be due to the formation, on the cleavage planes of the originally homogeneous γ iron solid solution, of needles of β iron. Normally such β iron would be obliged to expel the carbon which it had held in solution before the transformation, but, during quenching, time for such separation would not be available, and the β iron would be compelled to retain in "forced" solution, or in very fine suspension, the carbon thus unavoidably retained *in situ.* The "amorphous" theory also explains the hardness of quenched steel by postulating the existence of an

intrinsically hard but unstable transition product, which is formed when the transformation of the homogeneous γ iron solid solution into ferrite and carbide is hindered by quenching. Instead of identifying this hard substance with β iron, which has only a short range of stability in iron and low-carbon steels, the new (amorphous) theory ascribes hardening to the presence in the steel of amorphous layers similar to those which are believed to be the cause of the strain-hardening of ductile metals.[51]

Considering martensite as a cementite ferrosol, a colloidal dispersion of iron carbide in iron, it is "amorphous" in the sense that its particles, even if actually crystalline, are mostly not microscopically resolvable; and, especially in low-carbon steels on quick chilling, there is a tendency to carry over into the solid state some of the α-γ allocolloid or "β iron," so that the iron-dispersing phase itself may represent a colloidal dispersion, consisting mainly of minute α iron particles.[52] And because of the highly colloidal nature of the martensite and the consequent great development of free surface in it, it is extremely hard. Large percentages of oil colloidally dispersed or emulsified in water yield very firm stiff masses, although both phases are liquid.

Jeffries and Archer [53] say:

"There is no conceivable way in which a few per cent by volume of a strong constituent in disconnected particles could impart a new element of cohesion of the magnitude actually obtained. Their action must consist in rendering more effective the cohesion latent in the aluminum. The logical inference is that this is accomplished by the elimination of extended planes of weakness—that is, by slip interference. . . . Under the action of an external load tending to produce slip along these planes, the hard particles of $CuAl_2$ must act as *keys*, mechanically obstructing any motion along the planes as a whole."

This mechanical comparison will undoubtedly appeal to engineers, but *the action of surface forces*, together with fineness of crystal grain (which in itself reduces the length of any one plane of slip), are quite sufficient to account for the phenomena observed. In making putty the addition of a few per cent of oil makes a viscous, "strong" mass with whiting; the finer the "filler" the stiffer the mass it makes with the same amount of oil—i.e., the more oil it "takes." Again, as S. U. Pickering [54] showed, 99 per cent of petroleum oil emulsified in 1 per cent of soap water makes an extremely stiff mass.

These illustrations indicate that a few per cent even of a *weak* constituent may produce relatively great hardness, *provided that it is very finely dispersed*.*

This is quite contrary to what Jeffries and Archer state (page 1063): "We should not expect *soft* particles to produce hardening, because the 'keys' of soft substance would shear and thus assist rather than oppose slip. The term *soft* is used here in the relative sense only." Now, oil and water are certainly soft and scarcely act as "keys" that prevent slip in the cases above referred to. We must remember, however, that substances which are fluid *in mass* need not be so necessarily when finely subdivided. Thus the more finely divided mercury is, the more it seems to act like a solid. With increasing subdivision, surface forces ordinarily negligible predominate.[55]

Maximum Hardness Occurs at Less Than Maximum Dispersion.

The fact that austenite, though harder than pearlite, is not as hard as martensite, indicates that the latter represents a point, or rather a zone, of maximum degree of colloidality [56]—that is, there appears to be a certain degree of subdivision or dispersion, not necessarily the same with all substances, in which the dispersion system exhibits colloidal or surface phenomena to the

* See also discussion of the author's paper by Prof. Le Chatelier and my reply thereto—*Proceedings*, Am. Inst. Mining and Metallurgical Engineers, vol. 64.

highest extent, this effect declining not only with increasing aggregation or coagulation, but also with further peptization and the approach of true molecular dispersion, or the formation of smaller molecules.

Jeffries and Archer, in their paper on "Slip Interference," [57] designate the point of maximum hardness as the "critical dispersion." It had been referred to by Merica, Waltenberg and Scott.[58] In the preliminary paper on the zone of maximum colloidality referred to above,[59] it is stated:

"The *viscosity* of reversible, emulsoid, or hydrophile colloids, one of their marked characteristics, sometimes increases as the dispersed phase becomes *finer* (as in oil emulsions, homogenized milk) or sometimes as the dispersed phase becomes *coarser* (as with soaps, night-blue, butyric acid). In fact there seems to be with each dispersion a *zone of maximum colloidality,* above which viscosity decreases with coarser subdivision as the Brownian motion becomes sluggish (about 100 $m\mu$), and below which it also decreases as molecular dimensions are approached (about 5 $m\mu$), and the Zsigmondy-Brownian motion becomes violent. This zone has approximate limits and a crest or peak not necessarily the same with various substances—indeed we should expect specific variations.

"The approach toward the zone of maximum colloidality from the side of coarse dispersion is illustrated by clays which hold increasing amounts of water as their particles become smaller. The approach from the side of molecular dispersion is illustrated by the experimental results of Martin H. Fischer [60] on the sodium salts of the fatty acids. The sodium salts of formic, acetic, propionic, butyric and valeric acids always give molecular dispersions with water. Sodium caproate (with 6 carbon atoms) begins to show signs of "holding" water, while the caprylate (with 8 carbon atoms) gives a jelly when one mol is mixed with 250 cc. of water. With the higher acids in the series the water-holding capacity per mol of sodium soap increases rapidly as the molecules become larger: capric (C_{10}), 500 cc.; lauric (C_{12}), 4 liters; myristic (C_{14}), 12 liters; palmitic (C_{16}), 20 liters; margaric (C_{17}), 24 liters; stearic (C_{18}), 27 liters; arachnic (C_{20}), 37 liters.

"The appearance of a zone of maximum colloidality is not limited to the so-called emulsoid colloids. Thus with steel the Fe_3C-Fe dispersion reaches its maximum hardness in martensite, and becomes softer if the dispersion becomes greater (austenite) or less (troostite, sorbite, pearlite). A similar zone of maximum hardness exists in the dispersion of copper aluminide ($CuAl_2$)." [58]

The behavior of hypoeutectoid steels (containing less than 0.9 per cent C) is naturally complicated by the fact that the transformation of the excess γ iron (that in excess of the γ iron-cementite adsorption) into α iron, or the break-up of the α-γ adsorption ("β iron"), takes time and exhibits a lag which is most marked in the quickly cooled specimens. On the other hand, with hypereutectoid steels (containing more than 0.9 per cent C) the excess of cementite tends to crystallize out in slowly cooled specimens and to yield some undecomposed γ iron-cementite "solid solution" in quickly cooled ones. To consider these in detail, and also the high-carbon "cast iron," would unduly extend the limits of this paper; but I must comment on the observations of McCance,[61] who showed "that on adding carbon to iron, the hardness of the quenched steels increases up to 0.7 per cent C, and remains constant between this point and 1.18 per cent." This indicates a zone of maximum colloidal effect, which probably covers the zone of maximum degree of colloidality above referred to. The addition of manganese to steel, as Maurer has shown, retards the aggregation of the cementite so that ordinary slow cooling yields martensite, probably because the viscosity of the dispersion medium (iron) is increased by the manganese (melting point, 1,225 deg. C.), which by its surface or adsorptive action acts like a protector in opposing the aggregation of the martensite constituents; on the other hand, the manganese increases the speed of the transformation, when it finally does occur, because the manganese exerts its force then in the direction of the readjustment. Still larger percentages of manganese prevent any transformation at all, yielding austenite.

The literature is replete with metallurgical papers which educe facts consonant with or explainable by the fact that metals and alloys are prone to form colloidal dispersions. Among some of the reviews or books containing items of interest, the following may be mentioned:

Cecil H. Desch, *4th Report on Colloids, etc.* British Assocn. Adv. Sci., **1921.**

F. Sauerwald, "Kolloidchem. Technologie," Dresden, **1927**, pp. 675-698.

R. E. Liesegang, Kolloidtechnische Sammelreferate, XV, METALLE. *Kolloid-Z.*, **49**, 332 *et seq.* (1929).

George L. Clark, X-ray Metallography in 1929, *Metals and Alloys.* July-Nov. (**1929**).

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[2] Jerome Alexander, "The Importance of 'Impurities,'" *J. Soc. Chem.*, Jan. 15th (1917); *Ind. Eng. Chem.*, **15**, Feb. (1923).

[3] For results of ultramicroscopic examination of quickly and slowly chilled soaps, *see* J. Alexander, *Trans. Am. Inst. Min. Eng.*, 1919; *J. Soc. Chem. Ind.*, 1909; *Trans. Am. Inst. Chem. Eng.*, **2**, 210-228 (1909).

[4] Truly liquid metals have a low viscosity. *See* abstract of Prof. T. Turner, *J. Soc. Chem. Ind.*, **40**, 190R (1921).

[5] *Z. Elektrochim.*, **10**, 502 (1904).

[6] So do soft metals; lead and tin, for example.

[7] *See* H. Bechhold, "Colloids in Biology and Medicine," translated by J. G. M. Bullowa, New York, D. Van Nostrand Co., **1919**, p. 52.

[8] "Colloids and the Ultramicroscope," translated by J. Alexander, New York, John Wiley & Sons Co., **1909.**

[9] *J. Am. Ceramic Soc.*, **2**, 261-281 (1919). Randall, Rooksby and Cooper [*Trans. Soc. Glass Tech.*, **14**, 219 (1930)] showed by X-ray data that glasses and "amorphous" bodies consist of crystalline particles, the order of size being 10^{-6} to 10^{-7} cm. That is, they are colloidal (10 to 1 mμ). In silica glass (vitreous silica) they estimate the *average* crystallite contains about 20 molecules.

[10] *J. Am. Ceramic Soc.*, **2**, 313-322 (1919).

[11] "Colloids and the Ultramicroscope," p. 65. E. A. Schneider anticipated Zsigmondy, whose discovery, however, was made independently.

[12] *Physik. Z.*, **25**, 45 (1924).

[13] *J. Am. Chem. Soc.*, **41**, 1010 (1919).

[14] Scheerer, *Nachr. Ges. Wiss. Göttingen*, **96**, 100 (1918); *Chem. Abstracts*, **13**, 2624 (1919).

[15] *J. Am. Inst. Metals*, 11, 300-324 (1917). See also *J. Inst. Metals*, **20**, p. 109 to 140, and *Trans. Am. Inst. Min. Eng.*, Bull. 146, February, 1919.

[16] Pope and Barlow. The intrinsic weakness of the crystal lies in its tendency to rupture along lines of slip or cleavage.

[17] As Graham said, colloids possess energia.

[18] Dr. G. H. Gulliver, *J. Inst. Metals*, vol. 20, p. 158 (1918).

[19] Alexander and Bullowa, "Archives of Pediatrics" (1910).

[20] J. Alexander, *Kolloid-Z.*, **4**, 86 (1909). See also his paper in Vol. I of this series.

[21] J. Alexander, *J. Soc. Chem. Ind.*, **28**, 280 (1909).

[22] J. Alexander, *Kolloid-Z.*, **4**, 86 (1909).

[23] A mixture of Na_2CO_3 and NaCl crystallized in the presence of gelatin may form a "flowering plant," the Na_2CO_3 forming gracefully curved "stems" and the NaCl characteristic four-petaled "flowers."

[24] *J. Soc. Chem. Ind.*, **28**, 280 (1909).

[25] See P. Longmuir, *J. Iron and Steel Inst.*, September, 1907; *J. Soc. Chem. Ind.*, **26**, 1064 (1907).

[26] *J. Soc. Chem. Ind.*, **26**, 614 (1907).

[27] *See also* Beilby, *Proc. Roy. Soc. (London)*, **79**, 463; *J. Soc. Chem. Ind.*, **26**, 926 (1907).

[28] *See* C. Benedicks, *Métallurgie*, **5**, 41 (1908); *J. Soc. Chem. Ind.*, **27**, 406 (1908).

[29] Carnegie Research Reports, *J. Soc. Chem. Ind.*, **27**, 570 (1908); F. Wüst, *J. Soc. Chem. Ind.*, **26**, 412 (1907); Hersey, *J. Soc. Chem. Ind.*, **27**, 531 (1908).

[30] "Introduction to Physical Metallurgy," p. 249.

[31] Rosenhain and Ewen, *J. Inst. Metals*, **8**, No. 2 (1912) and **10**, No. 2 (1913). Rosenhain and Humphrey, *J. Iron and Steel Inst.*, **1913**, I.

[32] Rosenhain, *Engineering*, October, 1913. *Interni. Z. Metallog.*, **5**, 1914.

[33] Heyn, "Report on Progress of Metallography from 1909 to 1913," Internatl. Testing Assocn., N. Y. Congress, 1912. Tammann, *Z. Elektrochem.*, **18**, July (1912). Guertler, *Internl. Z. Metallog.*, vol. 5, 1914.

[34] W. E. S. Turner ("Molecular Association," p. 99) says: "The formula of a substance shall be recognized as a function of the physical conditions under which it exists, so that the formula for elements is X_n, for compounds $(XY)_n$, where n is to be specified according to the conditions. Although we are far from realizing how n varies for most substances, the adoption of such formula would bring home clearly the fact that both the physical and the chemical behavior of a substance may be closely dependent on the value of n." *See also* his paper in Vol. I of this series.

[35] *See* paper by P. Niggli, *Kolloid-Z.*, **10**, 268, entitled "Colloid Chemistry and Twin Crystals."

[36] See "The Action of Mercury on Steel at High Pressure," *Proc. Am. Acad. of Arts Sciences*, **46**, 325-341 (1911); also subsequent papers.

[37] "Introduction to Physical Metallurgy," p. 170.

[38] *J. Iron and Steel Inst.*, No. 2 (1912). *See also* his paper in this volume.

[39] The so-called Haeussler alloys are magnetic, although their constituents individually are not.

[40] *Chem. & Met. Eng.*, **24**, 1059 (1920).

[41] See also p. 1065 of Jeffries and Archer's paper.

[42] In the presence of protective colloids, insoluble salts (i.e., $CaCO_3$) become more soluble in water.

[43] Rosenhain, "Introduction to Physical Metallurgy," p. 175.

[44] The higher the temperature before quenching, the longer the cooling time, and therefore the greater the degree of aggregation.
[45] *J. Iron and Steel Inst.*, No. 2, 1912; *Kolloid-Z.*, **7**, 290 (1910).
[46] *See also* Benedicks' paper in this volume.
[47] *Engineering,* vol. 107, p. 341 (March 14, 1919).
[48] J. Alexander, *J. Soc. Chem. Ind., loc. cit.* (1909); Alexander and Bullowa, *J. Am. Med. Assocn.*. **55**, 1196-1198 (1910).
[49] J. Alexander, *J. Am. Ceram. Soc.* (1920), "Ultramicroscopic Examination of Some Clays."
[50] Faraday and Beilby did this by floating gold leaf on cyanide solutions. *J. Soc. Chem. Ind.* (1903).
[51] Rosenhain, pp. 180-182.
[52] Jeffries and Archer, *Chem. Met. Eng.*, **24**, 1065 (1920), have shown with the X-ray spectrometer that quick chilling can save some of the iron in γ form.
[53] *Chem. Met. Eng.*, **24**, 1061 (1920).
[54] *J. Chem. Soc.*, **91**, p. 2002 (1902).
[55] See "Surface Tension and Surface Energy," by E. Hatschek, 2nd Ed., **1919**. On page 28 *et seq.* is a discussion of phenomena in metals.
[56] This is the subject of a preliminary paper, since published, *J. Am. Chem. Soc.*, **43**, 434 (1921).
[57] *Chem. Met. Eng.*, vol. 24, p. 1057.
[58] "The Heat-Treatment of Duralumin," Bureau of Standards Bull. 150 (1919).
[59] It is interesting to note that the sun repels particles of colloidal dimensions, although smaller ones as well as larger ones are attracted. *See* J. Alexander, "Colloid Chemistry," D. Van Nostrand Co., 1919, p. 37.
[60] Fischer, *Chem. Eng.*, vol. 27, pp. 155-62 (1919).
[61] "A Contribution to the Theory of Hardening," *J. Inst. and Steel Inst.*, 1914, No. 1, p. 192.

Colloidal Conditions in Metal Crystals *

By Prof. Dr. W. Guertler,

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Colloidal conditions in crystals—dare such an expression be generally employed? Are not the concepts "crystalline" and "colloidal" so opposed that it is impossible to conceive of anything colloidal within a crystalline body?

Since the space lattice is not merely a theoretical conception, but as the result of practical X-ray research has become a demonstrated fact, it is known that the interior of crystals is built up of atoms that fill the entire volume in all three dimensions by millions and billions, along similar straight lines at some fixed distance apart, depending upon the nature of the particular atom. In compounds composed of different elements, the atoms alternate in accordance with definite regularity; in most cases the concept of the molecule disappears entirely. Each atom is bound as firmly to its left-hand as to its right-hand neighbor, while within the entire crystal no smaller entity exists than between the crystal and the atom itself.

There is a wide range of crystalline solutions. These have been subjected to experiment, in many cases with the result of transferring to their behavior the laws of the statics and kinetics of the liquid state. But in this work a limit was soon encountered, beyond which such a transfer was no longer possible. It must be remembered that there is only one liquid state, but that there are very many different crystalline conditions recognizable according to the type and character of the space lattice. This lattice may be built up in simple (i.e. cubic, rhombohedral, triclinic, etc.) units or very complex ones. Each of these forms has its own laws, more particularly those dealing with the physical properties; metallurgically most important, however, are those governing the mechanical properties.

At this point, it must be acknowledged that the statics and kinetics, and in general the entire physical chemistry, of the crystalline state are as yet only in the first stages of their development. Investigators are endeavoring to penetrate from many directions into what is really universal darkness. But in order to accustom ourselves to it, it will first be necessary to abandon the old dogma that has been adhered to for so many centuries—"*Corpora non agunt nisi fluida.*"

On adding to a crystal consisting of a pure element or a pure chemical compound, definite amounts of another substance, it may now be stated with certainty that there will not develop as in liquid solutions, sometimes colloidal, sometimes true solutions; in these solid solutions, on the contrary, the nature of the space lattice necessitates a definite but quite different classification. Provisionally, it appears that three distinct possibilities must be distinguished:

(1) The dissolved atoms can replace, atom for atom, those of the original element or original compound. This seems to take place in the structure of normal solid solutions. Thus on adding nickel to copper, nickel atoms enter atom for atom into the space lattice, by displacement of copper atoms from

* **Translated by Dr. Jerome Strauss, Bridgeville, Pa.**

their positions. Or in the case of a chloride, whose crystals are built up on a space lattice of regularly alternating atoms of metal and chlorine, an addition of a bromide of the same metal can effect the replacement, one after another, of chlorine atoms by bromine atoms. But the modifications that the space lattice undergoes thereby, especially the expansion or contraction of the spacings, cannot be entered into here.

(2) The added atoms can also enter the space lattice under such conditions, that not a single one of the original atoms is thrown out of its position. The former place themselves, so to speak, in the empty spaces—the openings between the original atoms. This appears to be the case in the assimilation by metal crystals of certain non-metals, especially such as possess no chemical affinity for the metal atoms.

(3) Finally, the added foreign atoms can be firmly held in definite positions by the metal atoms of the space lattice; somewhat as the moon is held by the earth and constrained to revolve about it. Where an atom previously stood there is then found, so to say, an atom with a moon; consequently, there has been formed a closed system of several atoms and, therefore, something that can be regarded as a molecule.

In these three fundamental types there also appear transitions difficult to align with any of the fundamental types.

Within an alloy particularly complex conditions may be encountered, as, e.g. in the alloy system aluminum-copper. Both metals crystallize in the cubic system with the so-called face-centered space lattice. The space lattices of the two metals differ only in their atom spacing. On adding to one metal a small amount of the other, there results type (1)—atom by atom displacement. This continues, however, only up to a definite small limit. In copper the amount of aluminum present cannot materially exceed 9 per cent, while in aluminum the amount of copper cannot greatly exceed 5 per cent at elevated temperatures and 1 per cent in the cold without producing quite a new lattice arrangement.

If the two metals are associated in other proportions, crystals of completely different space lattice occur. There is one type of crystal that is of tetragonal form within which two aluminum atoms associate with each copper atom. These crystals can obviously be spoken of as chemical compounds. In another type, of rhombohedral construction, one copper atom is always associated with each aluminum atom. Here also the term chemical compound is justified. To a third type the chemical formula Cu_2Al has been assigned. But by precise experiments it is found that this atomic ratio is not invariant; it fluctuates between 17:9 and 9:4. X-ray investigation shows that the basic structural unit, the so-called unit cell of this crystal, is composed of 52 atoms. This number of atoms (52) cannot be apportioned into whole numbers of copper and aluminum atoms, especially not in the proportion of 2:1. This space-lattice is also face-centered cubic, yet it is evident from the above that its structure is entirely different from those of copper, aluminum, and their solid solutions. Finally, there exists a fourth type of compound to which the formula Cu_3Al has been applied, despite the occurrence of insignificant variations in composition. It also is face-centered cubic. Since this crystal type exists only at elevated temperatures, it has not been thus far satisfactorily investigated. In instances such as these it is doubtless impossible to speak of a true chemical compound.

The preceding concise introductory remarks are simply to make clear what follows.

With many alloys it has been found that by alteration of temperature one

crystal type may be formed from another, i.e. one space lattice may be converted into another. In such cases there arise transition states which exhibit a certain parallelism with the colloidal state in liquid solutions. Just to mention one example: the gold-copper alloys crystallize from the molten state in the form of a continuous series of solid solutions. Within certain composition ranges, however, upon cooling to a definite temperature, the cubic space lattice of the solid solution gives way to crystals having the tetragonal lattice of a compound. Of frequent occurrence and technically important is the case where a saturated solid solution, because of a drop in solubility with a drop in temperature, precipitates a corresponding quantity of the dissolved substance. An outstanding example is found in the solid solutions of copper in aluminum, above mentioned.

Let us examine this case a little more closely. If it were to be dealt with as a series of liquid solutions, there would exist in these solutions from the very beginning free atoms or molecules of aluminum, free atoms or molecules of copper and finally undissociated molecules of actual compounds such as $CuAl_2$ and CuAl with possibly also other compounds such as Cu_9Al_4, $Cu_{17}Al_9$, Cu_3Al (see above) included with them, all existing together in definite dissociation and reaction equilibria, which are, in known manner, dominated by the law of mass action. Under certain conditions these compounds might separate as crystalline precipitates, leading to formation of emulsions, suspensions, colloidal solutions, etc. But in the interior of solid solutions the conditions are entirely different. The precipitates form within the more or less rigid, crystallographically-oriented space lattice. The question arises whether the precipitate must primarily adapt itself to the space lattice of the mother crystal, or whether from the outset it is free to adopt the different space lattice typical of crystals of the precipitate. Since it has at present been satisfactorily established that the former view is correct and that the new space lattice forms later; the further question arises: when and how is the change consummated? If the initial precipitation occurs in atomic or nearly atomic dispersion, conditions exist which undoubtedly are in many respects analogous to those in colloidal solutions.

Now the colloid state is one of extraordinary importance. Intermediate between the initial state expressed by the original undistorted space lattice, and the final state representing a completely formed precipitate which developed into microscopically visible crystal particles, there lies somewhere a state involving the best mechanical properties, with high strength and malleability, which in metallurgical practice has been designated as the enriched * ("veredelte") or more recently as the maximal-hardened ("ausgehärtete") condition. The heat treatment necessary to attain this objective is comparatively easily established for any particular alloy. The fundamental principles are known. It is becoming more and more evident that the majority of technical alloys, strictly speaking, belong to this enriched or maximal-hardened class. To attain this optimum condition in a suitable alloy, it is first heated to a sufficiently high temperature to secure complete saturation of the solid solution by the added substance; then by rapid cooling precipitation is inhibited, for otherwise precipitation would naturally take place as cooling reduces the limits of solubility. A supersaturated condition is thus preserved. Three cases must then be distinguished:

(1) Even the most rapid cooling possible may not be able completely to

* The German "veredelten" is not rendered by "ennobled" because this connotes making an alloy behave like a so-called noble metal, e.g., gold. The English expression generally employed for what is referred to here is "precipitation-hardening." Since the way the original was framed made it inexpedient to use this expression, "enriched" has been used throughout the translation.

suppress the precipitation. In this case, the transition condition corresponding to enriching forms during the quenching and is preserved. Among phenomena belonging in this group is the hardening of steel.

(2) Precipitation during quenching may, initially, be completely suppressed, but later, on long standing at room temperature, say for several days, the precipitation may take place to such an extent that the enriching makes itself apparent. The precipitation-hardening of duralumin is typical of this group.

(3) Thirdly, quenching may lead to indefinite stability at ordinary temperatures, with no appearance of precipitation and enrichment, although this phenomenon follows subsequent treatment at elevated temperature. This is spoken of as heat-hardening (Warmveredelung), hardening by reheating (Warmhärtung), or maturing by reheating (Warmreifung); and the greater number of modern hardenable (veredelbarer) alloys are of this type.

Invariably, before reaching the enriched state, an alloy first passes through a transition state, where the precipitation is scarcely, and in most cases never, microscopically visible. There is involved, therefore, an ultramicroscopically fine dispersion, a state to which the term "colloidal" may be and is justly applied.*

The time required to reach and then over-shoot the zone of maximum hardness depends upon the temperature chosen for heat-hardening. The absolute value of the maximum hardness also depends upon the temperature selected. In order to attain the greatest enriching effect and consequently the optimum colloidal condition, it is necessary to keep within prescribed limits of tempering temperature and tempering time.

Because of the tremendous technical importance of the problem, a special branch of science with every available means of research has endeavored to throw light upon the mechanism and consequences of these precipitation processes, unfortunately with very little success so far.

As to practical results, however, it is gratifying that great strides have been made. In the domain of steel hardening, which only recently has been considered as coming under the great group of metal-enriching materials and processes, these practical results have long been available. But the present development, now affecting in its rapid advance a wide range of alloy groups, involves more especially phenomena of type 3, as noted above.

According to the foregoing, the enriching treatment of this type is as follows:

(1) First the primary state, stable at the elevated temperature, is carefully produced by establishment of equilibrium.

(2) Then the metal is so rapidly cooled that there is no, or at least incomplete, transformation to the other state, stable at some lower temperature. By this means a state of unstable equilibrium is obtained.

(3) Finally, this unstable state is cautiously transformed (and up to now this is the only known means) by subjecting the material to a definite temperature for a definite time.

Each individual treatment of this type is characterized by a particular time-temperature diagram of the kind shown in Figure 1. Branch 1 of the curve represents the heating to the temperature corresponding to the first state, and branch 2 holding at that temperature for a sufficient length of time to produce equilibrium. Branch 3 corresponds to the adequately rapid cooling,

* For views as to the zone of maximum or optimum colloidality, not only in metals and alloys but also in other materials, *see* papers by J. Alexander in this volume and in Vol. I of this series, where references to earlier publications are given. This principle is also considered in several other papers in this volume, e.g., those of Spear, Shephard and Yap. J. A.

and branch 4 to the maintenance at room temperature, which, in many types of alloys, suffices to develop enrichment. Branch 5 represents the further heating to a temperature maintained over branch 6, the treatment being then concluded with a final cooling to room temperature (Branch 7).

The mechanical properties obtained vary according to the temperature and time of holding in branch 6. Thus, for example, hardness and compressive

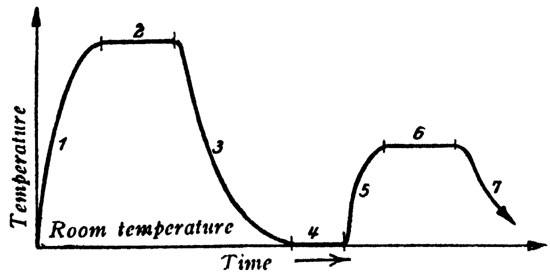

FIG. 1.—Heat Treatment Diagram.

strength, with increasing time at a given tempering temperature, pass through a maximum value, the magnitude and the instant of the occurrence varying with each temperature. Figure 2 shows schematically the dependence of the tensile strengths obtainable at various temperatures, upon the time spent in branch 6 (*see* Fig. 1), the tensile strength values appearing in Figure 2 as parameters. Curves of density, electrical resistance, etc., show equally important changes.

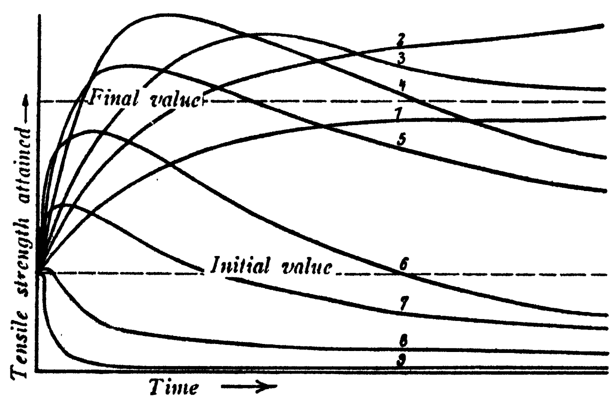

FIG. 2.—Example of the Relation of the Tensile Strength Obtainable by Enrichment, to Time and Temperature. (Compare with Fig. 1.)

Universal experience indicates that in the enrichment process we should never reach the temperature t_s at which lattice-mobility develops, this being in all metals about one-third the melting temperature.

Of great importance in connection with the foregoing is the practical utility of these methods in discovering alloys that will respond to enrichment and will offer the greatest possibility of successful treatment.

But whatever theoretical explanation may finally be reached, we are still far from a generally acceptable understanding of these phenomena. Instead,

therefore, of yielding to the temptation of presenting my own views, I will consider merely some aspects of the problem itself.

The problem is a physico-chemical one. It is therefore apparent that the same forces which maintain the atoms in their lattice positions may be mechanically considered as cohesion forces, or else chemically as affinities. But physical chemistry here leaves us completely stranded, for while we have a very detailed physical chemistry of the gaseous and liquid states, the physical chemistry of crystals is in the early process of development. We are thus thrown on our own resources. The statics and kinetics of the crystalline state are still to be developed; this applies even more particularly to the laws relating to the influences of temperature and time. They are important not only in order to comprehend the ordinary properties of metals and alloys but more especially in order to deal with the problems of strengthening and recrystallization; they are of primary importance in explaining the mechanism of enrichment.

As is known, in the formation of a new crystal type from one previously existing, there have heretofore been generally recognized only two factors:

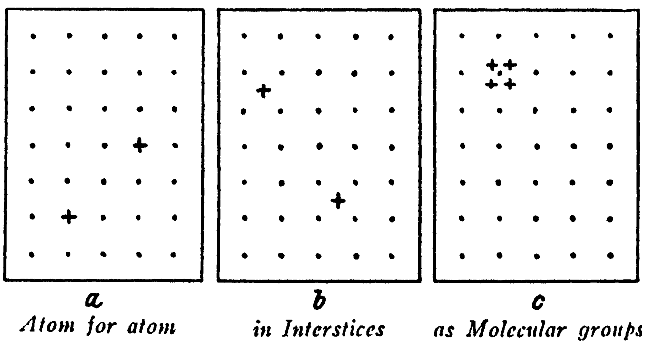

FIG. 3.—Three Types of Space Lattice Produced by Additions to a Solid Solution.

precipitation and growth, or nuclei-formation and the speed of recrystallization. However, in my opinion this twofold aspect alone is not entirely satisfactory, if each single step of the evolution is carefully envisaged.

(1) Considering first the initial state and particularly the exceptional case, which is undoubtedly represented by all instances of enrichment thus far known, we find that this initial state is monophasic and in equilibrium. Of course the three different types of this initial state previously noted must be recognized. In Figures 3 a to c these are assembled intentionally at random, namely, first, a replacement of both types of atoms, atom for atom (Fig. 3a), secondly, the placing of the added foreign atoms in the interstices of the space lattice (Fig. 3b) and lastly the formation of molecular groups at individual points of the space-lattice (Fig. 3c).

It is of course possible that in one and the same alloy several of these three types may arise, and that one type in the initial state may go over to another at the start of enrichment or transformation to a multiphasic system.

(2) The initial state can therefore be followed by a preliminary regrouping. This may occur either in the sense noted immediately above and represented in Figures 4 a and b; or with alloys composed of more than two constituents, as illustrated in Figures 5 a and b in which two added types of atoms migrate toward each other and together form the beginning of a mole-

cule. The second case is differentiated from the first in that it is not possible without interchange of positions by the atoms, and is, therefore, limited by the minimum temperature permitting diffusion processes within the crystal. Even more complicated are structures such as that of the well-known compound Al_6Mg_4Cu in aluminum.

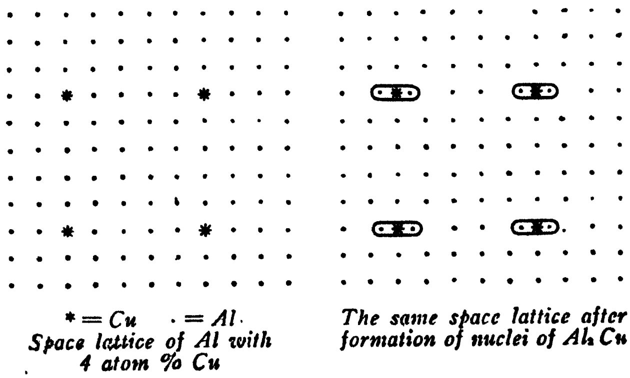

FIG. 4.—Rearrangement of Space Lattice by a New Crystalline Phase which Forms Nuclei.

(3) The next step that can occur is the inception of the formation of individual crystals of the precipitated second phase. In order to make clear what is meant by this, it is necessary to consider briefly the crystallization of a substance from the amorphous or liquid state. Take as an example a cubic crystal of a simple type. In three-dimensional space, there are six space lattice

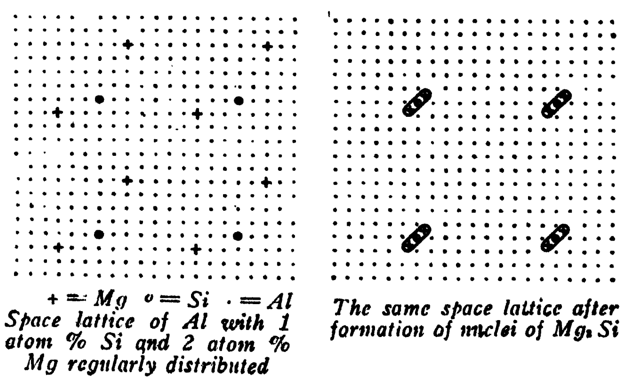

FIG. 5.—Rearrangement of Space Lattice by Germination from Two Different Additions.

bonds for each atom. In the amorphous state all of these bonds are unsatisfied. This state is 6/6ths (i.e. entirely) amorphous (refer to Fig. 6a). Two atoms by joining having created the origin of a space lattice structure, one bond of the six belonging to each atom becomes satisfied (Fig. 6b). The condition represented is then only 5/6ths amorphous. When four atoms have joined together, the resultant condition is 4/6ths amorphous (Fig. 6c). Upon the meeting of eight atoms it is reduced to only 3/6ths (Fig. 11d), while further consideration readily indicates that, by the meeting of three

times three times three atoms, it is only 2/6ths amorphous (Fig. 6e). Thus, a relationship is established between the proportion of crystalline matter and the number of atoms in the edge of the unit cube as is shown in the curve of Fig. 7; there is first a steep rise and then a rapid approach to the limiting value asymptotically; this is applicable to microscopically visible crystals, which on the outer surface have unsatisfied and therefore still amorphous-type bonds.

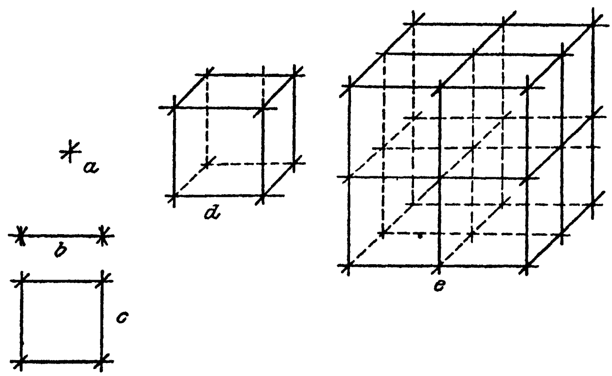

FIG. 6.—Continuous Transformation from the Amorphous to the Crystalline State.

If this view is transferred to crystals that form from the material of other crystals, it is seen that in the transformation from the second to the third condition defined above there exists a continuous progression, indicative of an initially very intensive, and later an asymptotically maturing, change of state. This view should only serve to point toward the fact that at low temperatures at which atom movement is still difficult, the simultaneous ejection of, shall

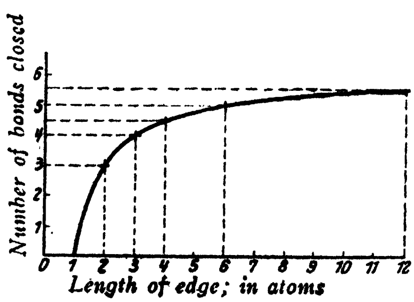

FIG. 7.—Relation of the Proportion of Satisfied Lattice Bonds to the Crystal Size.

we say, 27 billion individual and still "amorphous" atoms (or molecules), can be sharply differentiated by the influence upon various properties from the precipitation of one billion minute crystals with but three atoms per cube edge in a 2/6ths "amorphous" state. *The increase in the number of precipitated new structural units influences the properties undoubtedly in a different manner than does their individual growth with steady or decreasing number;* in the last case the hypothesis of a partial re-solution or else a splitting up of the particles cannot be overlooked.

(4) As soon as the newly formed crystalline units have become visible the enrichment, according to our empirical knowledge, has been past; that is, the desired maximum value of hardness and tensile strength have been lost again. In this connection, it is important to keep in mind what is known from the appearance of innumerable segregated structures, namely that the atoms ejected from a mother crystal arrange themselves at once in planes along the clearage planes of that crystal and therefore appear when cross-sectioned in a micro-section, as typical segregated needles; in the photomicrographs, Figures 8 and 9, examples of this structure, are shown.

FIG. 8. FIG. 9.

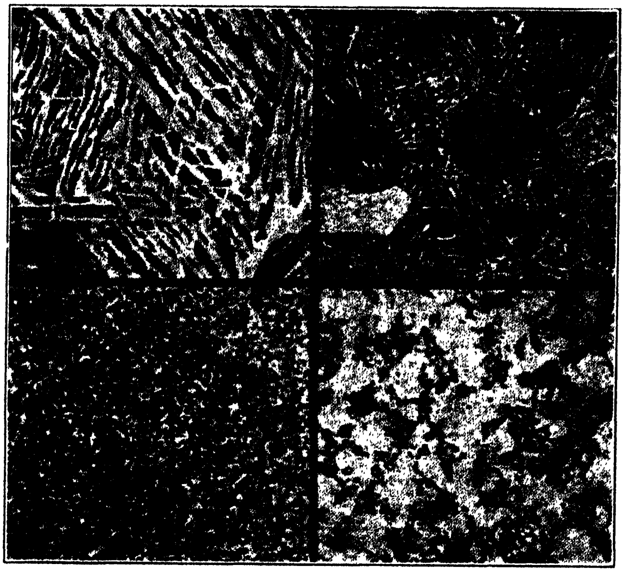

FIG. 10. FIG. 11.

FIG. 8.—Fe plus 0.7 per cent C; etched with alcoholic HNO_3-150x (reduced ½ in reproduction).

FIG. 9.—Brass with 0.12 per cent Pb, 0.03 per cent Fe; etched with copper ammonium chloride, 36x (reduced ½ in reproduction).

FIG. 10.—Fe plus 0.75 per cent C; first heated to 900° C., water-quenched, and then heated to 700° C.; etched with alcoholic HNO_3. 600x (reduced ½ in reproduction).

FIG. 11.—Steel with 0.3 per cent C; etched with picric acid. 600x (reduced ½ in reproduction).

(5) First with increasing mass the new crystal type is able to manifest its own crystallographic pattern and later forms itself into rounded grains or other individual figures (*see* Figures 10 and 11).

With this very fine grain size, therefore, there is associated a great decline in the number of unsaturated lattice bonds. Thus for example, a group of 64 atoms with $6 \times 64 = 384$ such lattice bonds, if precipitated from a mother crystal, would have as a long string of single atoms, 258 unsaturated bonds; as four-atom segregated plates, 160 unsaturated bonds; as four-atom-edged cubes finally, 96 unsaturated bonds.

Summarizing the above conditions 1 to 5 it can be seen that no satisfactory explanation is yielded solely from the simple twofold division: nuclei-formation and rate of recrystallization or precipitation and growth. The manner in

which these five concepts are arranged in succession may lead to differing views regarding their significance. Here belongs that frequently met but as yet unexplained term *"Incubation Period."*

From the above it is apparent that it is in the nature of things that no research procedure is likely to be as efficient as X-ray methods for space lattice analysis, in throwing light upon the enrichment process. Only these methods can answer the question of what are the initial state and the state of unstable equilibrium resulting from rapid cooling, what changes are produced in the latter by heat treatment, and particularly at what step of this transformation the maximum value of the desired mechanical properties may be retained. Besides this, of course, there are a whole series of physical properties, principally electrical conductivity and volume, which are available to aid in the clarification of this phenomenon that is so complicated and as yet so confused and full of contradictory isolated facts.

Colloid Systems in Metallography

By Carl Benedicks,

Director of the Metallographic Institute in Stockholm.

Summary of Previous Work.

Troostite.

It was a rather striking fact that Felix Osmond,[1] when describing the micrographic constitution of the system iron-carbon, found so many constituents (metarals) as the following: ferrite, cementite, pearlite, sorbite, martensite (and hardenite), troostite and austenite (in the order given by Osmond).

Some of these metarals were easy to interpret: ferrite is the homogeneous α-iron which is stable at low temperatures; cementite is the homogeneous carbide Fe_3C. Pearlite is the heterogeneous eutectoid mixture of ferrite and cementite, with an eutectoid carbon content of 0.9 per cent; the only objection which has been made is that of J. O. Arnold,[2] who considered this as being a sub-carbide $Fe_{24}C$. Sorbite (which is always accompanied by pearlite) was characterized by Osmond as being "pearlite which has not been able to separate into ferrite and cementite by reason of lack of time or from other cause." The metarals martensite, and also austenite, which occur after quenching, were later on recognized as being solid solutions, in α-iron, and in γ-iron respectively. Troostite was described by Osmond as a dark etching constituent occurring as soon as the quenching velocity is less than that necessary for the retention of martensite. As to the nature of troostite, a proliferating discussion was held at the beginning of this century. Thus it had been predicated: Troostite is a constituent occurring in a stable condition at a temperature interval below the critical point; troostite is pure β-iron; troostite is α- or β-iron containing elementary carbon; troostite is γ-iron containing carbon, and so on.*

However, it was pointed out by C. Benedicks [3] in 1905, that all the known facts regarding troostite were at once understood if we consider this metaral as being a metallic *solid colloid system,* composed of ultramicroscopically small cementite particles dispersed in α-iron. According to this, troostite occupies an intermediate position between martensite and pearlite.

Accordingly we understand that, as stated by Osmond, in order to produce troostite the quenching velocity must be less than for obtaining martensite; the great susceptibility to attack by reagents, largely exceeding that of the homogeneous solid solution martensite (as well as austenite), and that of the microscopically heterogeneous mixture pearlite, is a consequence of the extremely great development of the interface between the submicroscopic cementite particles and the iron, giving rise to a strong electrolytic action (by local elements). This attack of the (endothermic) cementite results in the formation of elementary carbon, or of some organic product, giving a dark color to the surface, with few perceptible details. Further, we at once obtain an

* For details, *see* C. Benedicks.[4]

explanation of the fact that troostite preferably occurs in those parts of the martensite which are adjacent to ferrite (in hypo-eutectoid steels) or to cementite (in hyper-eutectoid steels); as a matter of fact either of the free constituents must act as a nucleus for the separation (splitting up) of the solid solution.

As for the colloid hypothesis of troostite—which is now generally accepted, it must be borne in mind that J. O. Arnold [2] already in 1896 had expressed the view that troostite was nothing but an "emulsified carbide present in an extremely fine state of division." As Arnold at the same time expressed another view, namely that the black areas which correspond to troostite were actually "sub-carbide of iron, $Fe_{24}C$," we easily realize that the former hypothesis passed without exerting much influence.

E. Heyn and O. Bauer [4] in 1906 studied the action of dilute sulfuric acid on steel specimens, reheated to different temperatures. On account of a sharp maximum corrosion, or solubility, of the specimen when reheated to 400° C., they were led to predicate the existence of another constituent which was called *osmondite;* this, naturally, would signify a sharp limit between martensite and troostite.

C. Benedicks [5] in 1908, however, pointed out that this maximum solubility stands in full harmony with the colloid hypothesis: osmondite, as defined by Heyn and Bauer, must be the state of a quenched carbon steel specimen when possessing the colloid character in its purest form (in other words, when containing a maximum content of troostite). It was shown by experiment that in the same way the homogeneous solution phenol-water, on cooling, passes a colloid state before coagulating, which is characterized by a sharp maximum of the opacity; both properties (solubility, opacity) are functions of the development of the interface between two phases.*

At the same time a number of cooling speed determinations were communicated which present some interest for the formation of the colloid state. The cooling was characterized by the time corresponding, for a given steel specimen, to the fall in temperature from 700° to 100° C. It was found that, with $\tau = 3.07$ to 6.2 sec, the given carbon steel (containing 1.0 per cent carbon) consisted of martensite; on slower cooling with $\tau = 9.5$ sec, it consisted entirely of troostite. The photographically registered cooling curve gave evidence that in the latter case the evolution of heat on cooling, which is designated as recalescence, had taken place—as is the case for pearlite, while in the case of the quicker cooling no such evolution of heat was observed.

It was also found that the specific volume, and the specific electric resistance of troostite (0.12777 cm.^{3}; 18.1 microhms per cm.^{3}) are identical with those of pearlite, and differ considerably from those of martensite (0.1285 to 0.1293 cm.^{3}; 37.2 microhms).

These facts gave further evidence that troostite behaves as a pearlite with ultramicroscopically small cementite particles, or as a *cementite-ferrosol.*

A noteworthy circumstance was also the following (C. Benedicks): [6]

It has been known for a considerable time that steel when possessing its greatest strength and toughness, contains troostite; thus, in the manufacture of rails there has been an effort to produce a troostitic product. This signifies that the metallurgist, when highest elasticity and toughness were desired —without knowing it himself—*has aimed at obtaining the steel in a colloidal state.* Just as the sinews of the organic world are colloids, the "sinews" of the inorganic world—tempered steel wire—have a colloidal character.

* This indicates that there is a zone of maximum colloidality. *See* papers by J. Alexander and A. Einstein in Vol. I of this series. J. A.

Nickel-iron.

In the same paper it was further pointed out that a colloid system—which possibly stands in some relation to the well-known tenacity of the nickel-steels —occurs in the iron-nickel alloys. As a matter of fact, even in practically carbon-free iron-nickel alloys, where no separation into two constituents had been discernible microscopically, the electrical resistance figures gave evidence that a separation must have occurred. It had been proved earlier (C. Benedicks [7]) that, on slow cooling, a microscopically visible separation into two phases, as in meteoric iron, does occur, though, earlier, the Fe-Ni alloys were considered to be homogeneous solid solutions. Thus, it was highly probable that even in the case of iron-nickel-alloys the colloidal state was of some importance (*cf.* C. Benedicks).[8]

As other possible instances of the occurrence of colloidal systems in metallography, the following were adduced. On slow cooling, especially when silicon is present, cementite is dissociated, giving a graphite which is designated as temper carbon. A colloidal intermediate state with submicroscopic graphite particles would not improbably be found to exist.

Copper-aluminum.

To judge even now from some photograms published by H. C. H. Carpenter [9] a colloidal constituent does occur in the copper-aluminum alloys.

In 1913, A. Portevin [10] laid stress on the fact that the β-constituent of the aluminum bronzes occurs in conditions of widely different fineness. *Compare also* H. Hanemann and P. Merica.[11]

As a matter of fact, in copper-aluminum alloys, a lamellar constituent ($\alpha + \delta$) is to be observed which presents a close analogy to pearlite. At several spots one also sees a constituent where no details are visible. This is apparently the analog of troostite, or is such a constituent with submicroscopic particles.

Other Instances.

A. Lottermoser,[12] 1911, pointed out the interesting fact, that upon comparing R. Zsigmondy's theory of the formation of gold ruby glass with the above theory of the nature of troostite, a complete analogy is found in every point.

As a matter of fact, on the occasion of a discussion with H. Le Chatelier,[13] this analogy had already been noticed by C. Benedicks.[14]

An important contribution to the knowledge of colloidal systems in metallography was made by H. C. H. Carpenter [15, 16] in 1912, with reference to the so-called β-constituent in copper-zinc alloys. This "is to be regarded below 470° C. as an extremely minute and uniform complex of α and γ particles. Its structural stability is so remarkable that even after six weeks' annealing at 445° C., no appreciable coalescence of these particles has been observed in an alloy of exactly the eutectoid composition. When, however, a few crystallites either of α and γ are initially present in an otherwise pure eutectoid alloy, then, on annealing at 445° C., this stability is comparatively easily destroyed. These crystallites constitute nuclei for the deposition of α and γ, as the case may be."

As seen from this, there is a close analogy between this β constituent and troostite; quite remarkable is the influence, in both cases, of the presence of nuclei: on the formation of troostite (α-iron, cementite), and on the separation, or resolution, of the β-constituent (into $\alpha + \gamma$-phases). As a matter of

fact, on the presence of nuclei, the primarily unresolvable β-structure was in a short time transformed into a coarse structure, where, even to the naked eye, α has a pale gold, γ a bluish gray color.

In a later investigation, H. C. H. Carpenter [17] aimed at finding out some addition to the (apparently homogeneous) β-constituent which would make it still more stable. No such additional element was found; instead it was discovered that the β-structure was strengthened by removing foreign elements as completely as possible. This remarkable result can scarcely represent any general rule.* Usually, the interval friction, or viscosity, of a solid metal—which opposes the separation into two phases, is increased considerably by foreign elements.

The importance of colloid chemical points of view for metallography were further recognized by some leading colloid chemists. P. P. von Weimarn,[18] in 1912, dealt with the influence on the electrical conductivity of the degree of dispersion of one metallic phase in another. The degree of dispersion was defined as being the ratio W/V, where W is the surface area and V the volume of the dispersed substance.† It was considered that the internal surface area was responsible for the additional resistance of solid solutions and its comparative independence of temperature. W. Guertler,[19] in introducing this paper, justly expressed some doubts as to this view.‡

W. Guertler,[20] in 1912, directed attention to the fact that in the aluminum-zinc alloys, as investigated by W. Rosenhain and S. L. Archbutt, parallels occur to troostite and sorbite. Also for the tin-cadmium alloys, Guertler [21] reproduced structures of similar character.

W. Guertler, later on, in a part of his text-book which was published in 1913,[21] gave a very clear and detailed review of the discussion on the nature of troostite.

On the Possible Colloidal Nature of Acetate-copper.

In 1913, the view was put forth by T. R. Briggs [22] that copper which has been obtained electrolytically from a solution of acetate—Schützenberger's "allotropic copper"—is to be regarded as *colloidal copper,* or as a compact hydrogel of the normal metal.

As a matter of fact, it is universally admitted that several metals can be obtained as *gels* by the coagulation of their *sols.* Thus, the yellow form of silver described by Carey Lea § which is obtained by the reduction of silver tartrate (or other salts) is now recognized as being a hydrogel.||

By analogy, Briggs now claims that this "allotropic" copper represents a colloidal state; thereby it is held that "a gelatinous, colloidal substance, probably copper hydroxide formed by a hydrolytic decomposition," acts as a "protecting" colloid.

This view is of considerable interest to our subject but cannot be considered as definitely established. "Allotropic" copper had been studied in detail by C. Benedicks [28] (in 1906); it was found that the "allotropic" copper contains considerable quantities of organic substances, and the conclusion was drawn that the difference between this "acetate-copper" and the regular copper was

* It is an instance of the importance of impurities. J. A.

† It might be remarked that this definition ceases to apply when atomic dimensions are approached.

‡ In any event for troostite, the resistance comes very near that of the coagulum, pearlite, as we have already seen. We will here add that if there is to be any rational ground for stating that, in a given case, colloid chemistry affords an elucidation of matters, it is necessary to demonstrate the existence of an *intermediary state*—of a maximum or minimum, or discontinuity of a property curve—when passing from atomic dispersion ("true solution") into the coagulated state (with two distinct phases).

§ Carey Lea, *Am. J. Sci.,* 3, 37, 476 (1899) and following.

|| *Cf.* R. Abegg und Fr. Auerbach, "Handbuch der anorganischen Chemie," II: 1, Leipzig, 1908, 736.

due to the occurrence of impurities in solid solution.* This view was supported by W. Guertler,† who directed attention to the fact that certain explosive metals presented an analogous faculty of retaining non-metallic substances in solid solution.

We might epitomize the difference of opinion in the following way:

1.—Briggs assumed the metallic copper to be the dispersed phase (with some "protecting" non-metallic substance as dispersing phase).

2.—Benedicks, on the other hand, assumed the non-metallic substance to be the dispersed substance (occurring in true solution or as less finely dispersed phase, with metallic copper as the dispersing phase).‡

The author still adheres to the second view, as being the more probable one, for the following main reasons:

1. According to Briggs' hypothesis, we would expect acetate-copper to be nearly non-conducting for electricity, in the same way as Lea's silver is "non-conducting, or nearly so." §

Instead, acetate-copper has a very considerable conductivity (resistance was found to be 6 to 10 microhms per cm./cm.^{2}) which is of the same order as that of the metals cadmium and iron, and even exceeds that of tin or palladium.

2. As the coalescence of copper particles on heating (of a short duration) to as low a temperature as 200° C. is rather imperceptible, it follows that according to Briggs' hypothesis, when a piece of acetate-copper is heated so that the organic substance is removed, the adhesion between the metallic particles would be considerably lowered, and the substance would become extremely brittle. This is by no means the case.

3. Generally speaking, according to Briggs' hypothesis, the brittleness of acetate-copper would be much greater than that actually observable. Thus it was easy to cut out and handle small strips, e.g., of the dimensions 21 × 1 × 0.5 mm. (still preserved in good condition!). This certainly is not possible with Lea's colloidal silver.

4. The very considerable state of stress, or contraction tendency, which manifests itself in the acetate-copper, seems to be much easier to explain under the assumption of a supersaturated solid solution than otherwise.

Though, according to this, the present writer does not consider the colloid hypothesis of acetate-copper as being the best one, the matter certainly still deserves attention.

Further Publications.

Wo. Ostwald,[24] in 1915, consecrated part of his book "Die Welt der vernachlässigten Dimensionen" to the review of the dispersion chemistry of alloys, and reviewed the question also in his *Kolloid-Zeitschrift*.[25]

A review of the question was also given by J. Alexander [26] in 1920. This author expressed the view that while austenite might be a solid solution, martensite is a colloid system. This, however, is not in accordance with facts already mentioned. As a matter of fact, we must consider martensite as well as austenite as being a solid solution, martensite in α-iron, and austenite in γ-iron. On the other hand, we may state that between the solid solution

* As a possible alternative the author suggested that the dispersion of the organic substances might not (always) be so high as to correspond to a "homogeneous" solid solution, but that the acetate substance might be present as a dispersed phase in the copper, so that the acetate-copper was an "acetic cuprosol."

† W. Guertler, "Metallographie," Bd. I: 1, Berlin, 1912, p. 59.

‡ T. R. Briggs, *loc. cit.*, p. 292.

§ T. R. Briggs, *loc. cit.*, p. 292.

martensite and the colloid system troostite there is no really sharp demarcation. As well known by metallographers, the martensite needles which occur in austenite frequently present all kinds of coloring on etching, from a very weak to a very dark one, and this according to all probability is due to a continuously proceeding coagulation into troostite.*

Finally, C. H. Desch,[27] in 1921, has given an excellent report on colloidal systems in solid crystalline media, embracing metallic and other solid bodies.

General Remarks.

Occurrence of Metallic Colloid Systems.

In view of the extremely frequent occurrence of colloids with ordinary liquids as the dispersion medium, it is striking how comparatively few have been observed with a metallic dispersion medium. This, however, seems to be due entirely to the very much greater difficulty of studying them in the latter case.

As a matter of fact, under other, similar conditions, the apparent stability of a colloid system must increase with increasing *viscosity* of the dispersion medium. Thus, in a solid metallic medium, owing to its high viscosity, colloid states are to be expected to be of a comparatively frequent occurrence.

The condition which is generally to be fulfilled for the formation of a metallic colloid system can be formulated as follows:

Suppose we have a homogeneous solution of two components. On account of the change of a variable factor—generally a drop in temperature—the mutual solubility decreases. A separation (splitting up) of the homogeneous solution into two phases will then take place. Before the two phases are microscopically separated, an intermediary, more or less stable, colloidal state must occur.

The greater the viscosity (or in general the lower the temperature), and the less the mutual solubility, the greater will, generally speaking, be the apparent stability of this highly dispersed intermediary state.

Accordingly, as a rule, *a colloidal state will occur after cooling through any eutectoid* † *point;* on the contrary, it will be much more difficult to observe in connection with an *eutectic* point, on account of the lower viscosity at higher temperatures.

The possibility, or facility, of actually observing microscopically this intermediary state, will depend on the question, whether or not the two phases concerned differ considerably in their electrochemical position, being consequently differently attacked by reagents. Thus, the great facility of observing troostite is due to the fact that the submicroscopic cementite particles are easily decomposed and blackened by acids. A difference of color between the two phases will facilitate the microscopic observation of a colloid constituent. On the other hand, if the difference in susceptibility to attack and in color is an insignificant one—as, e.g., in the case of iron-nickel—the colloidal state will be difficult to observe.‡

* *See* Alexander's paper in this volume. Since martensite is *microscopically* resolvable, it is obviously at the upper border of the colloidal zone, the unresolvable hardenite and austenite being finer colloidal dispersions of cementite. Some particles of colloidal dimensions may occur in coarser dispersions, and in general there is no uniformity of particle size; *some* molecularly dispersed cementite may well be present in *every* other phase. J. A.

† "Solid-eutectic."

‡ Particles well within colloidal dimensions are not even visible in the microscope, and solid metals do not lend themselves to ultramicroscopic examination. Furthermore, etching agents may destroy the structure originally existing, yielding misleading artifacts. For ultramicroscopy of *pyrosols, see* R. Lorenz' paper in Vol. I of this series. J. A.

Systematization of Metallic Colloids.

In the former part of this paper no analysis has been made as to the different types of colloidal systems which might be said to occur in metallography. Such a systematization, however, is indispensable for their further treatment, and will be attempted here.

The two phases belonging to a colloidal system, namely the *dispersing phase* (or medium), and the *dispersed phase* (or medium), can be solid, liquid and gaseous; we will designate these states as for the dispersing phase with S,L,G, as for the dispersed phase with s,l,g.

We then obtain the eight following general types (the last type Gg being excluded, as two gaseous phases cannot coexist): *

Possible Types of Colloid Systems.

No.	Character of Dispersing Phase	Character of Dispersed Phase
1	S	s
2	S	l
3	S	g
4	L	s
5	L	l
6	L	g
7	G	s
8	G	l
9	G	g)

Now, for each of these possible general types, three cases may be distinguished: (*a*) Both phases metallic; (*b*) dispersing phase only metallic; (*c*) dispersed phase only metallic.

We will affix an M and m respectively in order to indicate that the phase concerned is metallic. Thus, a metal hydrosol, say produced using Svedberg's method, is to be designated as representing type Ls_m.

For metallography, type S_Ms_m is that which primarily must be considered, but evidently a number of the other types might also be of some importance. A short general review of the different types containing at least one metallic phase is therefore attempted in the following, in the order indicated.

Short Review of the Different Types Possible.

Type *Ss*. Type S_Ms_m, as already pointed out, is the one most frequently met with in metallography. Example: troostite ($M = \text{Fe}$, $m = \text{Fe}_3\text{C}$). The systems Fe-Ni, Cu-Al, Cu-Zn give other illustrations.

Type S_Ms is represented by finely divided non-metallic inclusions ("sonims") in metals, say iron oxide in iron. In spite of the important rôle slag inclusions play from a practical point of view, very little is known about this type.

Type Ss_m is represented by the alkali chlorides, containing finely dispersed alkali metals,† or by the ruby glasses, containing gold, silver, copper, etc., dispersed in a glass.

Type *Sl*. (A system S_Ml_m would possibly occur in a fine-grained metal, quickly heated just to its melting point, as the melting generally begins at the grain corners; especially when the metal is not pure, the liquid phase would eventually occur in a highly dispersed state in the solid metal.)

* A similar schedule is to be found in R. Zsigmondy, "Kolloidchemie," Leipzig, 1912, p. 25.
† According to T. R. Briggs (*vide supra*) the acetate-copper would belong to this type.

A system $S_M l$ could possibly be considered as a transition form in the acetate-copper (*cf.* above). As a matter of fact, it has been found (C. Benedicks [28]) that an acetic liquid sometimes is ejected from the acetate-copper; * if this observation is correct, it seems probable that, under certain circumstances, a transitory colloidal state might occur.

Type *Sg*. Type $S_M g$ probably plays a rather prominent rôle in metallurgy, viz., in the occurrence of minute gas inclusions in solid metals. On account of a greater solubility in the liquid phase, a gas content is likely to form minute blow holes in the solidified metal. The contraction blow holes in a quickly cooled antimony might be considered to be of this type.

Type *Ls*. Type $L_M s$ presents a considerable practical interest. Minute non-metallic slag particles, dispersed in molten iron, demand a careful study on account of the great metallurgical importance of eliminating slag inclusions.

In this direction some remarkable results, not yet published, have been obtained by P. Sederholm, working in the Metallographic Institute at Stockholm under the author's direction. It was discovered that it is possible mechanically to obtain a kind of "amalgam" or metallic mercury paste, containing as much as, say, 50 per cent of finely dispersed mercury oxide. The appearance is entirely metallic. The product has the striking property of being extremely sensitive to even very small amounts of impurities, for on grinding, these cause a separation or coagulation of the oxide. Otherwise, nothing is known as to the coagulation of metallic colloids (*cf.* Desch,[27] p. 35).

Type Ls_m has been known since a very long time. The *aurum potabile* of the alchemists—so frequently dealt with in earlier literature—was apparently nothing but a finely dispersed gold-sol. The metal suspensions which were produced mechanically by J. Langelott † with the aid of the "philosophic mill," or the metallic colloids as prepared by Bredig and Svedberg, belong to this type.

Type *Ll*. Type $L_M l_m$ occurs when two metals possess a critical temperature above which the liquid metals are miscible in all proportions; on cooling, an intermediary system $L_M l_m$ will probably be formed—for a colloidal state *Ll* is well known for the non-metallic system phenol-water. The systems lead-zinc and bismuth-zinc behave in this way, as was discovered by W. Spring.‡

Type $L_M l$, or a suspension of a non-metallic liquid in a molten metal, is probably possible to observe—say with sulfide of iron in iron. The type Ll_m is represented by the "pyrosols" formed at high temperature electrolysis, and described by R. Lorenz; [28] e.g., lead in chloride of lead.§

Type *Lg*. Type $L_M g$, or a gas emulsion in a molten metal, might have a considerable practical interest.

Types *Gs* and *Gl*. The systems Gs_m and Gl_m occur, according to the temperature, as "metal fog" ("Metallnebel") on several occasions, as on electrical disintegration of metals—already observed by Faraday—or as in the well-known metallization process, invented by M. U. Schoop. (The solid metal formed by this process might partly be reckoned as belonging to type $S_M g$, because it contains gas.)

This short review gives evidence that there is a vast field for further research along these lines!

* *Cf.* C. Benedicks,[28] Fig. 18.

† J. Langelott, "Epistola ad Praecellentissimos Naturae Curiosos. De quibusdam in Chymia praetermissis." Hamburg, 1672.

‡ W. Spring and L. Romanoff, *Z. anorg. Chem.*, 13, 29, 1897.

§ H. Moissan found that on adding small amounts of platinum to mercury, the mixture would "emulsify" with water. *See* paper on Pyrosols by R. Lorenz in Vol. I of this series. J. A.

Additional Remarks.

In an exposition of the present character it might be expected to find mentioned the so-called "amorphous metal" introduced by Sir George Beilby.* However, as the present author has stated previously,† there are, according to his view, other possibilities for explaining the facts related, which are more probable than the assumption of an amorphous metal phase.

Further, on account of the high dispersion, surface tension plays an important rôle in colloidal systems. It would then be natural to consider here the views of G. Quincke ‡ regarding the foam structure of metals. The author, however, does not consider the connection with colloid chemistry to be close enough here to justify an analysis of this metallographic question.

Later Additional Remarks.

During recent years, the type $S_M s_m$ has been much discussed in connection with the successive hardness increase discovered by Wilm [28] in duralumin, and occurring also in other alloys, when kept at room temperature after a quenching say from 500° C.[29] The theory was advanced by Merica, Waltenberg and Scott [30] that the successive hardness increase was due to the formation of a finely dispersed precipitation, Al_2Cu, the maximum hardness being assumed to correspond to a certain critical dispersion of the precipitate. This "dispersion hardening" theory was adopted by Jeffries and Archer,[31] Harder [32] and others. A great number of researches has been devoted to this matter.[33]

The idea that a colloid system, at a certain dispersion should be harder than the supersaturated solution from which it is formed is contrary to the general fact that greatest hardness observed, as in the case of hardened steel. occurs generally in supersaturated solutions (as martensite), the hardness diminishing as soon as a colloid system (as troostite) is formed.[34] It also is contradicted by the fact that the increase in hardness is accompanied by an increase in electrical resistivity, while the precipitation assumed would cause a decrease in resistivity.[35] The actual existence of such a critical dispersion in no way has been established. Instead the facts observed seem to be explained in the following way.

In the original solid solution of a metal A, containing a certain amount of an element B dissolved, immediately after quenching the atoms B may simply —say in a statistical way—substitute atoms A in the lattice. The solid solution then does not need to be supersaturated, and it is not much harder than the pure metal A. Now, in all cases of "dispersion hardening" a special compound, having a low solubility in A, has been admitted to be formed successively—as in duralumin the compound Al_2Cu, or other compounds. Consequently, we may admit that on ageing at a conveniently high temperature the atoms B may combine with (i.e. in a definite way rearrange around them) atoms A, forming, in a given case, a compound A_nB, which, as already said, possesses a low solubility in A. Hence, the solid solution may now be supersaturated as the amount of elementary groups (or constellations) A_nB increases on ageing; consequently, it will be characterized by a great hardness.

Simultaneously the electrical resistivity may be expected to increase, since the groups A_nB may differ from the atoms of the A-lattice much more than the single atoms B.[36]

Accordingly, the "critical dispersion" may be viewed as representing the

* *See* G. Beilby, "Aggregation and Flow of Solids," London, 1921.
† C. Benedicks, "Sur la théorie Beilby de l'état amorphe des métaux," *Rev. Métal.*, 19, 505 (1922).
‡ G. Quincke, "Die Schaumstruktur der Metalle," *Intern. Z. Metallog.* 3, 23, 79 (1912).

state occurring, when the elementary groups A_nB—on account of the thermal agitation, and diffusion—have found time to form in the lattice of A.*

Observations, interesting from a colloid point of view, are given by K. S. Seljesater,[37] showing that arsenic may be considered as a retardent for the agglomeration of minute Sb particles in a Pb matrix. Similar considerations for Al-Si alloys by R. B. Deeley.[38]

Summary.

A review is made of the metallographic colloid system hitherto described. After some general remarks, a short exposition is made of the different types of colloid systems, containing at least one metallic phase; thereby a simple method is used for their systematic designation.

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36. As a matter of fact, dissolved atoms B cause a resistivity increase of a metal A all the more considerable, the more the atoms B differs from the atoms A. This was shown by C. Benedicks [*Jernkontorets Ann.*, 71, 35 (1916)] and by A. L. Norbury [*Trans. Faraday Soc.*, 16, 570 (1921)].
37. K. S. Seljesater, *Trans. Am. Inst. Mining Met. Eng., Inst. Metals Div.*, New York, **1929**, p. 573.
38. R. B. Deeley (ref.), *J. Inst. Metals*, **42**, 436 (1929).

* Supersaturated or supercooled liquids probably have in them a certain degree of molecular aggregation, analogous to that existing in gases approaching the critical state. (*See* papers by W. E. S. Turner and A. Einstein in Vol. I of this series.) Larger groups, whether they be formed by physical or by chemical aggregation, have diminished surface and kinetic activity; and the consequences of such decrease in surface and activity naturally follow. J. A.

On the Well-Known Five Structures in Carbon Steels

By Professor Kotaro Honda,

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A steel is heated above its transformation point (A_1 point) for a certain interval of time and then slowly cooled. This steel, when polished, etched with acid and examined under a microscope, shows a characteristic structure consisting of very fine alternate layers of cementite and iron or as it is called, "Ferrite." This structure is known as "Lamellar pearlite" or simply "Pearlite." The steel, when heated above its transformation point, has a homogeneous structure consisting of a solid solution of carbon in iron. When examined under a microscope, the structure should consist of an aggregate of a homogeneous phase separated by network boundaries. This structure is called "Austenite."

When a steel heated above the A_1 point is quenched in water, its hardness increases by more than three times that before quenching. This hardened steel, when polished, etched with acid and examined microscopically, shows a structure consisting of an aggregate of very fine needle-shaped crystals. This structure is called "Martensite." The martensite consists of well-defined crystals and is a homogenous * phase containing carbon in solid solution.

If the martensite steel be heated to a temperature of 250° to 300° C., the dissolved carbon is gradually precipitated as cementite particles (Fe_3C) from the steel and suspended as colloidal particles in the mother iron. The steel thus heat-treated, when polished and etched with acid, is colored dark, owing to the rough surface consisting of finely dispersed particles imbedded in ferrite ground, which is easily etchable. This structure is known as "Troostite." If the steel be further heated at 500° to 600° C., the coagulation of the colloidal particles of cementite gradually progresses, so that we can detect the grain with a high power microscope. Owing to the coagulation of the cementite particles, such a structure is not so easily etched by acid as the troostite, but it is much more easily etched than the annealed steel, and the structure, when etched with acid, appears bluish light dark. This structure is called "Sorbite."

If the heating takes place at a still higher temperature, say 600° to 700° C., the coagulation goes on still further and we obtain a structure called "Granular Pearlite." Thus, troostite, sorbite and pearlite (both lamellar and granular) are physically a mechanical mixture of ferrite and cementite, the only difference being the degree of coagulation of cementite particles.

So far we have in all five different structures usually observable in carbon steels. Of these structures, only three, that is, austenite, martensite and pearlite are physically different from each other. By means of X-ray analysis, it is shown that in austenite and martensite, iron-atoms have the configuration of a face-centered and a body-centered cubic lattice respectively. Austenitic iron or steel is generally non-magnetic, but not always so; for example, steels containing carbon in the vicinity of the eutectoid concentration are slightly

* Obviously, this means "microscopically homogeneous," electrons being, at present, the only particles not demonstrably heterogeneous. J. A.

magnetic for 30° C. above the A_1 point, that is, in the austenitic region. Nickel and nickel-carbon alloys have also a face-centered cubic lattice with respect to nickel atoms, and hence an austenitic structure, but they are strongly magnetic at room temperature. The iron (or nickel), which has a face-centered cubic lattice, is called γ-iron (or γ-nickel). Martensitic or pearlitic steel is always magnetic. The iron which has a body-centered cubic lattice, is called α-iron; α-iron is not always magnetic. For, δ-iron, which exists above 1,400° C., is now known to be the same as α-iron, but it is not magnetic. Thus the usual expression, "α-iron is magnetic" or "γ-iron is non-magnetic" are not correct. Magnetism is an atomic property and therefore may vary independently of the α or γ configuration of iron atoms.

Thus the nature of the three structures above referred to may be expressed by the following words:

Austenite is a solid solution of carbon in γ-iron, martensite that of carbon in α-iron, and pearlite (troostite and sorbite) is a mechanical mixture of α-iron and cementite.

This transformation is the change of structures consisting of austenite $\rightarrow$ pearlite, that is, solid solution of carbon in γ-iron $\rightarrow$ a mixture of Fe + Fe_3C.

Hence during cooling, the transformation consists of two changes:

(1) The change of the atomic configuration of iron from the face-centered to the body-centered;

(2) The separation of carbon atoms from the interspace of the lattice as cementite.

These two different processes take place very probably in succession, but not simultaneously; because in a natural phenomenon it is very difficult to consider two different processes as taking place exactly at the same instant. Admitting that these two processes (1) and (2) take place in succession, the next question is which of the changes (1) $\rightarrow$ (2) and (2) $\rightarrow$ (1) is more probable? The answer is obviously the change (1) $\rightarrow$ (2). For, if the change in the atomic configuration of the iron from the face-centered to the body-centered lattice is completed, the product is the α-iron dissolving carbon, but α-iron being unable to dissolve so much carbon, most of the carbon is precipitated as cementite. Hence, if the first change takes place first, the second one must follow as a necessary consequence; that is, the order of the changes (1) $\rightarrow$ (2) is very probable. On the other hand, the second change (2) cannot occur at the first step; because as the γ-iron has the property of dissolving so much carbon in it, it is very unreasonable to assume the sudden separation of the carbon to occur first without any change of the atomic configuration.

If the above view regarding the order of the successive changes is assumed to be correct, the process of the A_1 transformation, that is, austenite $\rightarrow$ pearlite consists in γ-iron dissolving carbon $\rightarrow$ α-iron dissolving carbon $\rightarrow$ ferrite + Fe_3C, or austenite $\rightarrow$ martensite $\rightarrow$ pearlite. That is, the A_1 transformation in process consists of double or stepped changes, as we have already remarked. Thus the correctness of the stepped change is proved.

From the above consideration, the first change of the A_1 transformation is in reality the A_3 transformation, and hence the heat of this transformation, austenite $\rightarrow$ martensite, must be equal to that of the A_3 transformation in pure iron, a small allowance being made for the presence of the dissolved carbon atoms. Meuthen found by a careful experiment the heat of A_3 transformation in pure iron to be 5.6 calories; while N. Yamada measured directly the heat of the transformation, austenite $\rightarrow$ martensite, for a eutectoid steel and found it to be 5.7 calories per gram of iron. The agreement between these two is thus very satisfactory.

As we have shown, the A_1 transformation consists of the changes austenite $\rightarrow$ martensite $\rightarrow$ pearlite. This way of considering the A_1 transformation does not in the least interfere with the principle of the phase rule; because in the case of equilibrium, for which this rule is only applicable, the martensite is passed over and does not appear at all.

During a slow cooling, at the A_1 point, austenite first changes into martensite, and the latter changes immediately into pearlite, the result being the same as

$$\text{Austenite} \longrightarrow \text{pearlite.}$$

During a very rapid cooling, such as quenching in water, the change from austenite to martensite is so far retarded that it begins to take place at a temperature below 300° C., and when this change is completed, the specimen which is subjected to this treatment, is nearly at room temperature, and hence the second change from martensite to pearlite cannot take place, owing to the great viscosity of the specimen at room temperature. Thus martensite can be obtained by quenching the steel in water.

Since during cooling, the change from austenite to pearlite always occurs through an intermediate step—martensite—it is naturally assumed that during heating, the A_1 transformation, that is, the change from pearlite to austenite takes place through martensite, unless some contradictory facts are found.

According to the above view of quenching, the perfect hardening is obtained, when the first change in the stepped transformation, austenite $\rightarrow$ martensite, is completed and the second change, martensite $\rightarrow$ pearlite, is completely suppressed. In the case of a less rapid cooling, the first change occurs at temperature a little higher than in the above case, and therefore the second change partly takes place resulting in a martensite mixed with troostite. Since the hardness, H, of austenite, martensite and pearlite (troostite, sorbite) satisfy the following relation,

$$H_{mart.} > H_{pearl.,} > H_{aust}$$

the hardness of martensite mixed with troostite or pearlite is less than that of pure martensite. This is a case of imperfect hardening.

In the case of an extremely rapid cooling, not only is the second change completely suppressed, but even the first change is partially arrested. We then obtain a martensite structure mixed with austenite, the hardness of which is also less than that of pure martensite. This is a case of a too severe quenching. In such a case, however, cooling to the liquid air temperature which accelerates the change of the remaining austenite into martensite, increases considerably its hardness. That in a severely quenched steel, the austenite is present mixed with martensite, is actually confirmed by the X-ray analysis.

It is a well-known fact that in plain carbon steels, martensite can easily be obtained by quenching, but it is very difficult to obtain pure austenite by this means. This is easily understood from the fact that the first change, austenite $\rightarrow$ martensite consists in the mutual change of atomic configuration, while the second change, martensite $\rightarrow$ pearlite, is connected with the diffusion of carbon atoms through iron, so that the former change can take place even at low temperatures, but the latter cannot occur at room temperature. We thus see the reason why the pure austenitic structure is very difficult to arrest, while martensite can easily be obtained.

Several years ago, Dr. T. Matsushita showed that in carbon steels, there are two kinds of martensite, α and β, the α-form being more easily etched than the β-form. During a slow heating of a quenched steel, α and β martensites are tempered at about 180° C. and 300° C., respectively. X-ray analysis has

recently shown that α martensite is found only on the surface layer of the specimen and β martensite in the inside. The α martensite has a body-centered tetragonal lattice with an axial ratio 1.06, and the β martensite a body-centered cubic lattice, as above mentioned.

In the case of special steels, the velocity of the A_1 transformation becomes very small as compared with that in ordinary steels by virtue of the presence of other elements; hence even at the ordinary rate of cooling, the change, martensite $\rightarrow$ pearlite, may be arrested, so that we obtain the martensitic structure at room temperature. This is a case of a self-hardening steel.

Since the configuration of the iron atoms in martensite is the same or very near to that in α-iron, the question naturally arises why the carbon atoms in the interspace of the iron lattice give rise to such a great hardness as compared with that of α-iron. The following explanation is probably not far from the actual mechanism of the hardening.

The hardness of a quenched steel is affected by several factors; that is, the fineness of gram size, internal stress and the presence of carbon atoms within the lattice. It is a well-established fact that the hardness of a metal increases with the grain number, and that cold work resulting to internal stress causes also the hardening of the metal. The martensites consist of an immense number of extremely fine crystals, and also are undergoing a great internal stress caused by a rapid cooling during quenching. Again, carbon atoms in the lattice will send their lines of force toward six neighboring atoms and themselves behave like diagonal supporters in a rigid square framework, thus giving to the lattice building a great strength as a whole. Since the effect of grain size and that of internal stress on the hardness are fairly well known, it is possible to estimate approximately quantitative contributions of these factors to the hardness, that is, 80 in Brinell number for the grain size and 150 for the internal stress are probably not far from the truth. Assuming the Brinell hardness for a 0.9 per cent carbon steel quenched to be 680 and that for the same steel annealed to be 220, we get

Natural hardness of the steel	220
Increase due to grain number	80
Increase due to interstrain	150
Increase due to carbon atom within lattice	230
	680

It may be remarked that by quenching iron-nickel alloys containing about 15 to 30 per cent of nickel from the austenitic region into water or liquid air, a martensitic structure is obtained, and the hardness greatly increases, though no appreciable content of carbon is present. This is also explained in the same way as in the case of carbon steels. Above the A_3 line, iron atoms assume the distribution of a face-centered cube, some of them being replaced by nickel atoms according to the concentration, but below this line, they take that of a body-centered cube; the sides of the unit cubes in these two cases have a ratio of about 1:3. By quenching the alloys from the austenitic region into water or liquid air, the lattice changes from the face-centered cube to the body-centered, but owing to the very rapid cooling, some of the nickel atoms may not have a sufficient time to assume their proper position and may remain in the center of the face of the body-centered cube and play the part of carbon atoms in the martensite of carbon steels, thus giving to the alloys a great strength and great hardness.

The great hardness observable in martensitic nickel steels containing carbon requires no further explanation.

The Rôle of Surface Energy on the Equilibria of Iron and Iron Carbide

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It is the main purpose of this paper to call attention to the influence of particle-size of Fe_3C on the equilibria of the iron-carbon alloys, especially on the location of the A_{cm} line.* Considerable refinement in the experimental techniques of determining the A_{cm} points, has been evolved by metallurgical investigators, but they have neglected to take into consideration the influence of the particle-size of Fe_3C on its solubility in austenite (γFe). How great the influence of particle-size is on the solubility of inorganic salts in aqueous solutions has been shown by Hulett (Volume I, p. 637).

In connection with the writer's theoretical studies in the equilibria of the iron-carbon system,[1] he has noticed the disagreement in the results of various investigations on the A_{cm} line, as shown in Figure 1 below. The A_{cm} line No. 1 is one derived by the writer and the data for it will be published in the near future. It is noteworthy that the points obtained by Gutowsky all fall on curve No. 1, which the writer has good reason to believe is the most nearly correct one. It should be noted that all the points above curve No. 1 have been obtained by heating and cooling steels initially at room temperature, when Fe_3C already exists as a structural phase. All the points lying below curve No. 1 (with the exception of those points obtained by Carpenter and Keeling, which determine curve No. 3) have been obtained by annealing and quenching in order to differentiate the homogeneous from the heterogeneous field. Only the points obtained by Carpenter and Keeling were determined from the melt, in connection with their study of the liquidus and solidus lines of the iron-carbon system.

Although the various values obtained by the Japanese workers are somewhat discordant, yet their loci are all more or less parallel to curve No. 1 (Fig. 1), so that we may legitimately conclude that the disagreement is to be attributed merely to a temperature lag in the observed A_{cm} points.† The points obtained in the careful investigation of Wark involve annealing and quenching, and give an A_{cm} line of an entirely different slope (curve No. 2). The Carpenter and Keeling A_{cm} line (No. 3) present the least slope of the three curves shown in Figure 1.

The disagreement in the various sets of data (which fall into three classes, as it were) requires some explanation. It occurs to the writer that the influence of the particle-size of the iron carbide (Fe_3C) may adequately account for the disagreement. In the heat-treatment by Wark, the samples were first quenched to a fully martensitic structure (that is, heterogeneous structure in which Fe_3C is colloidally dispersed in the ferrite needles, containing perhaps a

* The A_{cm} line is a phase-boundary line, at which austenite, a solid solution, begins to precipitate Fe_3C upon cooling. The subscript (cm) stands for cementite, i.e., Fe_3C.

† It may be pointed out here that the influence of other foreign impurities at a constant molal concentration may raise or lower the A_{cm} line by equal temperature intervals.

small amount of carbide in solid solution) and then heated to successively higher temperatures until the structure is completely homogeneous, that is, austenitic. Hence, what we really obtain at any temperature, is the equilibrium

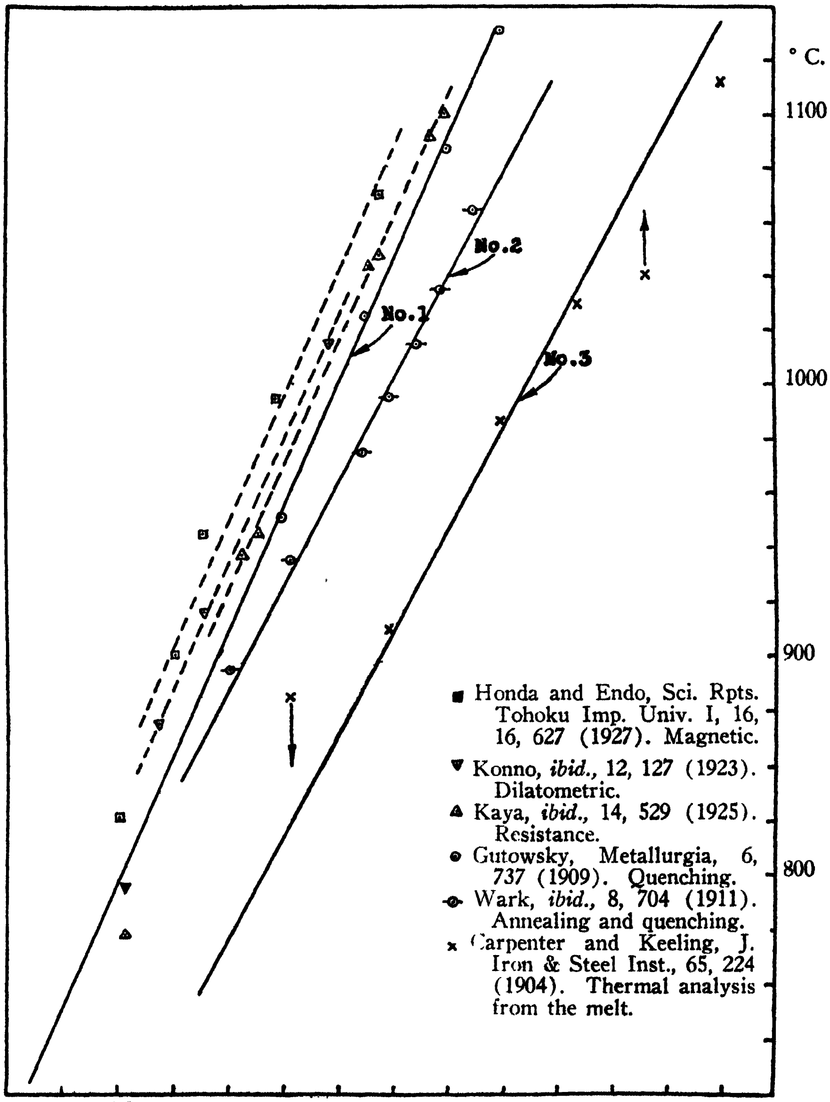

FIG. 1.—The A_{CM} line as determined by various methods of investigation. Only in the A_{CM} lines No. 2 and No. 3 is the influence of particle-size of Fe_3C likely to be involved.

between iron and Fe_3C particles well within the range in which particle-size affects its solubility—10^{-5} to 5×10^{-6} cm. in diameter.[2]

There are many fine points in the classical work of Carpenter and Keeling on the constitution diagram of the iron-carbon system, which strongly indicate

that in the range of temperatures lower than 1,200°C., their thermal data are quite reliable. Note in Figure 1 that their A_{cm} curve indicates a higher solubility at any temperature than is commonly accepted. The usual explanation, of course, has been that their samples were considerably undercooled before austenite began to precipitate Fe_3C. The undercooling is in turn attributed to the thermal hysteresis common to all transition in which a change of state (phase) is involved. Kaya obtained fairly reliable values, also by cooling down from a fairly high temperature to which the steel sample was heated, initially from room temperature, and his rate of cooling was about the same as that adopted by Carpenter and Keeling in their thermal studies. On the other hand, the A_{cm} line obtained by Wark (No. 2) is much lower than the A_{cm} line No. 1; and in this case, the method of experiment, involving annealing and quenching, reasonably excludes the probability of undercooling. In Wark's case, as well as in Carpenter's and Keeling's, however, the influence of the particle-size of Fe_3C appears to the present writer to be an important factor, and it is this viewpoint which will be emphasized in this paper. In Kaya's case, his steel samples contained only the normal Fe_3C plates (in pearlite) and the pro-eutectoid Fe_3C practically dissolves and precipitates *in situ* in the austenite grain-boundaries, and consequently the problem of nucleation and the growth of the crystal nuclei is not such a vital factor in determining the equilibrium temperature (A_{cm}).

The writer has shown elsewhere,[1] on thermodynamic grounds, that the solute in solid γFe (austenite) is elementary carbon; hence, when the steel cools down to the A_{cm} line, the first Fe_3C particles precipitated will be extremely small in size and they will tend to go back into solution. In this way, undercooling takes place easily, so that, for example, a 1.7 per cent carbon steel shows as much as 158° C. retardation in the A_{cm} point (Fig. 1). We shall discuss this matter at some length below.

Theoretical Discussions.

Inasmuch as Hulett's paper (*loc. cit.*) treats in some detail the historical development of the equations involved, we shall not repeat them here. We shall, therefore, only show the development of certain theoretical equations necessary to the purpose of this paper. The equation governing the relation of particle-size to super-solubility is generally given as

$$\frac{RT}{M} \ln \frac{s_2}{s_1} = \frac{2\sigma}{\rho} \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \tag{1}$$

in which RT has the usual significance, M is the molecular weight of the solute, s_2 and s_1 are the molal concentrations of the solutions in equilibrium with particles of radii r_2 and r_1 respectively, σ the surface energy, and ρ the density of the solid. In case the normal particle-size is large the surfaces would be planes and r_1 would then be equal to ∞, so that $(1/r_1)$ cancels out; s_1 would then be the normal solubility, which we shall hereafter designate as s_∞. (Also, arithmetically, as long as r_1 is large compared to r_2, the former can be safely neglected without appreciable error). Equation (1) then reduces simply to

$$\ln \frac{s_2}{s_\infty} = \frac{2M\sigma}{RT\rho r_2} \tag{2}$$

Equation (2) clearly implies that in a supersaturated solution of a given concentration at temperature T, there is a definite radius r which will be in

equilibrium with the solution—that is, there is an equilibrium particle-size. Towards larger particles, the solution behaves as a supersaturated one, but towards smaller particles, it behaves as an unsaturated solution.* It is, therefore, important to know the relation of the change in the equilibrium particle-size with respect to temperature. The van Hoff isochore as applied to the depression in the freezing point of solution is

$$\frac{d \ln s'}{dT} = \frac{-Q}{RT^2} \tag{3}$$

in which s' is the concentration at temperature T and $-Q$ is the molal heat of solution (or precipitation). Substituting the value of s' (or s_∞ in this case) in equation (2) we obtain

$$\ln s_{(T)} = \frac{2M\sigma}{RT\rho r} + \ln s_\infty \text{ or } = \frac{2M\sigma}{RT\rho r} + \frac{Q}{RT} + k \tag{4}$$

Suppose we now study the equilibrium conditions at some other temperature, $(T + \Delta T)$; then we will have a new equilibrium radius $(r + \Delta r)$ and correspondingly new values of $(\sigma + \Delta\sigma)$ and $(\rho + \Delta\rho)$. The new equilibrium will now be represented as

$$\ln s_{(T+\Delta T)} = \frac{2M(\sigma + \Delta\sigma)}{R(T + \Delta T)(\rho + \Delta\rho)(r + \Delta r)} + \frac{Q}{R(T + \Delta T)} + k \tag{5}$$

Since from the experiments of Laplace and others we know that as a first approximation, $\sigma/\rho = k$ (constant), we can, therefore, substitute ϕ for σ/ρ, as

$$\frac{\sigma + \Delta\sigma}{\rho + \Delta\rho} = \frac{\sigma}{\rho} = k$$

Imposing the condition that no precipitation (or dissolution) has taken place on account of the minute change in temperature, the right-hand side of equation (4) is then equal to the right-hand side of equation (5), so that we obtain

$$\frac{2M\phi}{RTr} + \frac{Q}{RT} = \frac{2M\phi}{R(T + \Delta T)(r + \Delta r)} + \frac{Q}{R(T + \Delta T)} \tag{6}$$

$$\frac{2M\phi}{Q} \mathcal{L}_{\substack{\Delta T \doteq 0 \\ \Delta r \doteq 0}} \Delta \left(\frac{1}{Tr}\right) = \mathcal{L}_{\Delta T \doteq 0} \Delta \left(\frac{1}{T}\right) \tag{7}$$

$$\frac{2M\phi}{Q} \int_{T,\infty}^{T',r} d\left(\frac{1}{Tr}\right) = \int_{T}^{T'} d\left(\frac{1}{T}\right) \tag{8}$$

which upon integration between the limits shown gives

$$T' = T\left(1 - \frac{2M\phi}{Qr}\right)$$

and upon substituting the proper value of ϕ reduces to

$$T' = T\left(1 - \frac{2M\sigma}{Q\rho r}\right)^{\dagger} \tag{9}$$

* This is the reason why, when we add to an undercooled solution minute particles of the crystal which will be precipitated from solution, crystallization (that is, precipitation) is often immediately induced. The particles which we add as nuclei of crystallization are probably always larger than the equilibrium particle-size for that particular temperature and concentration.

† The (—) sign should really be (±) depending upon the sign of the heat of solution.

in which T' is the temperature to which the solution can be undercooled without precipitation. As the particle-size increases, $\left(\frac{2M\sigma}{Q\rho r}\right)$ approaches zero, so that T becomes equal to T'.*

Equation (9) was first derived by Jones and Partington [3] in a somewhat different way, much less simple than that shown above. We clearly note that when the heat of solution is negative, that is, when the solute dissolves with an absorption of heat, the value inside the parentheses in equation (9) will be <1, so that undercooling can take place. If the radius of the nuclei is less than the equilibrium radius r, the temperature T' decreases without precipitation and the solution consequently becomes supersaturated. In such solutions the tendency to crystallization is extremely small at a low degree of supersaturation. The smaller nuclei (that is, $<r$) which could form comparatively easily due to molecular collisions, are unstable, however, and dissolve again immediately; the larger particles (that is, $>r$) which are stable, are not readily formed on account of their size, even in spite of the velocity of crystal growth.† According to equation (9) as T' decreases, the equilibrium particle-size r decreases similarly and the conditions thus become more favorable to the formation of a larger number of nuclei, so that when crystallization finally takes place, the crystallization velocity is large, as was demonstrated by the work of Miers and Isaacs in their study of labile solutions.

The Free Surface Energy of Iron Carbide (Fe_3C).

An attempt was made by Thompson [4] to measure the free surface energy of Fe_3C by approximating the degree of supersaturation from the change in the specific resistance of the steel samples. In this way, he obtained 1,350 dynes/cm. (or ergs/cm.^{2}) which, considering the extreme hardness of Fe_3C, seems too small. Aside from the fact that the theoretical basis of his calculations is open to serious question, he used a wrong equation, in which M (the molecular weight of the solute, Fe_3C) was omitted—his calculated value happens to be of the right magnitude, however. As Thompson's experimental data appear to be quite reliable, it might be of some interest first, to calculate on the basis of his results the magnitude of the free surface energy (interfacial tension) of Fe_3C. Thompson took two samples of a steel containing about 0.69 per cent carbon and quenched them from 780° C. Then he tempered one sample at 500° C. in order to make the structure finely sorbitic. The other piece was annealed for several hours at 650° C., as a result of which the Fe_3C particles were spheroidized. The specific resistances of these two samples (at 10° C.) were determined to be 17.87 and 16.73 microhms/cm.^{3} respectively. From these values he calculated the difference in solubility as 0.042 per cent carbon. He assumed the solubility in the second case to be about 0.02 per cent carbon at 500° C., so that s_2 (the solubility of the tempered piece) must then be 0.062 per cent. Since the specific resistances of the steels were measured at 10° C., we are really dealing with "equilibrium" conditions as obtained at that temperature and not at 500° C. as Thompson

* The writer is greatly indebted to Mr. H. De Wet Erasmus of the Union Carbon and Carbide Research Laboratories, Long Island City, New York, for checking the equations above and also for calling his attention to the interesting possibility of directly integrating the van Hoff reaction isochore between the limits $T, s\infty$) and T', s_2) and then combining the resulting equation with equation (2). The present writer has seriously considered this possibility, but has tentatively rejected it because it involves the assumption that the heat of solution is independent of the small particle-size and surface energy of the solute.

† In accordance with the extensive researches of Tammann, we may say as a generalization that there are two tendencies present in the solution as it is being cooled down from a high temperature, namely, nucleation and velocity of crystal growth.

would have it. The high-temperature treatment is merely to help the colloidally dispersed Fe_3C particles to aggregate to a size within the resolving power of the microscope. It is, therefore, necessary to calculate the solubilities of Fe_3C in ferrite at 10° C. (i.e., room temperature).

Yamada[5] has shown that the resistance of steel, R_E, at 20° C. can be expressed as a linear function of per cent carbon (C), thus

$$R_E = \alpha + \beta C$$

in which α, the specific resistance of pure iron, is 10.12 microhms/cm.³ and β has a value of 0.89. A steel containing 0.69 per cent carbon should then have a specific resistance of about 16.15 microhms/cm.³ As the annealed sample has a resistance of 16.73 microhms/cm.³, we may safely infer that the carbide particles must be appreciably dissolved in the ferrite. This should have been expected, because the particle-size of the finely spheroidized cementite is well within the range in which particle-size is a factor of solubility. Using Benedick's value (which Thompson quoted in his paper) of 2.68 microhms/cm.³ increase in resistance per 0.1 per cent dissolved carbon (carbide), the difference between 16.73 and 16.15 microhms gives 0.023 per cent carbon as the increase in solubility.* Accepting 0.007 per cent as the normal solubility of carbon in ferrite at room temperature,[6] the annealed sample, therefore, contained about 0.030 per cent carbon, and the tempered sample contained about 0.072 per cent carbon.†

The best datum[7] on the specific gravity of Fe_3C is 7.67. It remains to evaluate r_2 and r_1. Thompson gives 0.5×10^{-5} cm. as the radius of sorbitic cementite, which is, according to the work of Lucas,[2] a little low. It would be more accurate to assign 10^{-5} cm. to r_2, and the radius of the finely spheroidized cementite, (r_1), should then be of the order of 10^{-4} cm. Equation (1), upon substitution of all the proper values, then takes the form of

$$(8.32 \times 10^7)(283)\left(2.3 \log_{10} \frac{0.072}{0.030}\right) = 2\sigma\left(\frac{179.5}{7.67}\right)\left(\frac{1}{10^{-5}} - \frac{1}{10^{-4}}\right)$$

which, solving for σ gives

$$\therefore \sigma_{20^\circ \text{C.}} = 4{,}900 \text{ ergs/cm.}^2\ddagger \text{ (in round figures).}$$

The free surface energy of Fe_3C at room temperature (20° C.) is thus calculated to be several times the figure given by Thompson, which the writer had thought to be too low, considering its extreme hardness. On account of the small solubilities involved in the present case, the ratio of solubilities is susceptible to a fairly large error, but inasmuch as the value of r_1 may be a little low (as the exact period of anneal is not mentioned, and the longer the anneal, the larger the particle-size of the Fe_3C), the lower limit of the ratio of solubilities has been used in order to counterbalance it.

It would be interesting to study the nature of the equilibria obtained by Carpenter and Keeling in their determination of the A_{cm} line (No. 3 in Fig. 1) and incidentally calculate the surface energy from another source. From the "equilibrium" A_{cm} line (No. 1 in Fig. 1), we obtain at 1,136° C. $s_1 = 1.7$ per cent carbon and from the A_{cm} line of Carpenter and Keeling,

* Since the temperature coefficient of resistance is small, no appreciable error is introduced in comparing Thompson's values with values obtained at 20° C.

† The solubilities are so small that no error is introduced in not converting them to mol per cent. Fe_3C.

‡ Surface tension (expressed in dynes/cm.) is merely a hypothetical tension, invented as a mathematical expedient. The tension is conceived to be acting in all directions parallel to the surface. Hence, surface tension in dynes × cm² area is equal to surface energy in ergs/cm².

$s_2 = 2.1$ per cent carbon. Converting them to mol per cent we have 7.43 and 9.05 per cent respectively. Assuming that at 1,136° C. the specific gravity is about 7.3 and substituting all the necessary values in equation (2) we have

$$(8.32 \times 10^7)(1409)\left(2.3 \log \frac{9.05}{7.30}\right) = \frac{2\sigma}{r}\left(\frac{179.5}{7.3}\right)$$

$$\frac{\sigma}{r} = 4.7 \times 10^8 \text{ ergs/cm.}$$

If we know the correct value of r, we can easily derive the value of σ. Unfortunately equations (2) and (9) do not permit us to solve simultaneously the values of σ and r. However, if the Carpenter and Keeling A_{cm} line was really obtained under conditions which brought about undercooling, due to the extremely small particle-size of the Fe_3C precipitated, equation (9) should give us the same value of σ/r, that is, 4.7×10^8 dynes/cm. We must first calculate the heat of solution of Fe_3C in γFe. It can be easily shown that from equation (3) the following relationship can be derived:

$$\ln \frac{s_2}{s_1} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{10}$$

in which s_2 and s_1 are the solubilities at T_2 and T_1 respectively and Q is the heat of solution. From the "equilibrium" A_{cm} curve No. 1, we thus calculate Q to be about 4,900 cal./mol of Fe_3C precipitated.* Substituting all the necessary values in equation (9), including the value of T', which is 978° C. (Fig. 1), we obtain

$$1{,}251 = 1{,}409\left[1 - \frac{2\,(179.5)\,\sigma}{(4{,}900 \times 4.2 \times 10^7)(7.3)\,r}\right]$$

$$\frac{\sigma}{r} = 4.7 \times 10^8 \text{ ergs/cm.}$$

so that

which checks exactly the value derived previously. Equation (9) should, therefore, be very useful in determining the degree of undercooling possible, because if we substitute the value of (σ/r) obtained from equation (2) in equation (9), knowing, of course, the molal heat of solution of the solute involved, we can calculate T'. If we had done this above, we should have obtained T' as 1,250° (absolute) or 977° C. The temperature actually obtained is 978° C.

Thus it is shown, for the first time in a quantitative way, that the A_{cm} line obtained by Carpenter and Keeling differs materially from the normal A_{cm} line † because of the delayed precipitation of Fe_3C (with the consequent state of supersaturation) due to the influence of its high surface energy and fine particle-size. Equation (9) enables us to conclude that in Wark's case, the undercooling is much less, because the particle-size of the Fe_3C in his samples must be larger than that in Carpenter's and Keeling's experiments. That this is so may be inferred from the fact that Wark held his samples at constant temperature for some time before quenching.

* The value here thermodynamically calculated is at great variance with those derived from experimental data on the heats of reaction upon tempering steels quenched from different high temperatures. The nature of such reactions and the phases involved in the reaction are quite uncertain, and are consequently amenable to several interpretations. The writer has now in course of preparation a paper dealing with this subject.

† The Carpenter and Keeling A_{cm} line may, therefore, be considered as the *labile* solubility line and the A_{cm} line No. 1, the normal solubility line.

Let us approximate the surface energy at 1,136° C. From the work of Lucas [2] the radius of the Fe_3C particles well within the range of resolution of his microscope is, as stated above, about 10^{-5} to 5×10^{-6} cm.* The mean value, 7.5 (or, simply, 8) $\times 10^{-6}$ cm. may be safely used for the value of r, so that

$$\sigma_{1136^\circ \text{C.}} = (4.7 \times 10^8)\, r = (4.7 \times 10^8)(8 \times 10^{-6})$$
$$= 3{,}800 \text{ ergs/cm.}^2 \text{ in round figures.}$$

The calculated value of σ at 1,136° C. is consistent with the value calculated at 20° C., because we know that surface energy decreases as the temperature increases. An indirect method of checking the degree of reliability of the calculated values of σ is available, when we recall that the total surface energy, U, is a constant if we can reasonably consider σ as a linear function of the temperature. It can be easily shown by thermodynamics that

$$\begin{aligned} U &= \sigma + q \\ &= \sigma - T\frac{d\sigma}{dT} \end{aligned} \tag{11}$$

in which q is the latent heat of surface tension and is equal to $-T\frac{d\sigma}{dT}$. From the two values of σ calculated at 20° and 1,136° C., we obtain (approximately) $\frac{d\sigma}{dT} = -1$ erg/cm.^{2}/°C., with which we can calculate U in equation (11) thus

$$U_{20^\circ \text{C.}} = 4{,}900 + 293 = 5{,}193 \text{ ergs/cm.}^2$$
$$U_{1136^\circ \text{C.}} = 3{,}800 + 1{,}409 = 5{,}209 \text{ ergs/cm.}^2$$

The excellent check gives us some assurance that at least the calculated values of σ are of the right magnitude. The relative internal pressure calculated on the basis of these figures is consistent with the known internal pressures of Pt, Fe, Ag, Au, etc.

The total surface energy can be easily calculated from the change in the heat of solution of the solute. Hence, it should be comparatively simple to measure the heats of solutions of steels with spheroidized cementite of different particle sizes, and then calculate the total surface energy since we know the heat of solution of the normal lamellar pearlite at A_1.

Hardening of Metallic Alloys from the Standpoint of Surface Energy.

The writer feels it is not inappropriate to discuss briefly the probable influence of surface energy on the hardness of metallic alloys of the class which shows the phenomenon of precipitation hardening (e.g. the duralumin alloys). In recent years a number of theories of hardening have been advanced, mostly by metallurgists. On the one hand, we have the colloidal point of view represented by Alexander [8] and, on the other hand, we have the extremely mechanical point of view incorporated in Jeffries' and Archer's "slip-interference" theory.[9] The latter, while presenting a captivating picture of hard particles mechanically exerting a keying action that prevents slip in the grains

* This is the particle-size of the Fe_3C precipitated from austenite in quenched steels. The lower limit represents the particle-size of the Fe_3C upon tempering at about 100° C., so that 8×10^{-6} cm. is a reasonable radius to assign to the crystal nuclei obtained at a much higher temperature, 1,136° C.

of ferrite composing the matrix, has always been something less than satisfactory to the writer. Let us more pertinently discuss the hardness of martensite. According to the slip-interference theory, the minute cementite particles interfere with the slip of the ferrite grains, already minute. On the general theory of grain-size inheritance, the writer could never quite understand why the ferrite in martensite has ever been considered fine.* Recently, Heindlhofer and Bain [10] have shown conclusively that the ferrite grains are coarse. What remains of the slip-interference theory is the so-called "critical dispersion," indeed a happy phrase. Alexander evidently anticipated this in his theory of "maximum colloidality," defined as that state of aggregation in which the specific properties of a colloid are at a maximum.

According to the slip-interference theory, the interference is a purely mechanical action, while Alexander emphasizes the colloidal properties of a dispersed system, e.g., the high surface energy of a dispersed phase. In this, the writer subscribes to Alexander's point of view. The high surface energy of Fe_3C † shown in this paper can quite adequately account for the great hardness of martensite. If martensite is an enforced solid solution, as Honda has claimed for a number of years, the high degree of supersaturation should result in considerable distortion of the lattice. It is, however, extremely doubtful if any degree of distortion of the lattice could quite adequately account for the hardness of martensite. In the current controversy regarding the nature of martensite, the writer feels that the confusion arises from a misundestanding of the scope of the terms, martensite and troostite. Evidently these terms have been used to define the allotriomorphic forms of the structural phases present in quenched steels, rather than their actual chemical constitution (in terms of the phases present).‡ Thus the acicular structure of martensite is not a specific idiomorphic characteristic of martensite (as a phase), but is merely indicative of the rapid crystallization from an extremely labile solution. It is, of course, probable that in the transformation from a homogeneous phase (austenite) to a heterogeneous system (ferrite and Fe_3C), a transition phase is formed, which has the characteristics of a solid solution. This phase should be considered only as an extremely unstable mesomorphic state of martensite, and the writer prefers to call it *meta*-martensite.§ Upon the slightest tempering—even in the course of etching in boiling sodium picrate for microscopic examination, as was found by Lucas [2]—the *meta*-martensite precipitates the Fe_3C in colloidal dimensions, and this is the martensite we ordinarily observe under the microscope. We do not know at what stage of aggregation of the colloidal Fe_3C we obtain maximum hardness, but we do know that when the aggregation of the dispersed phase comes within the microscopic range, the system is not generally at its maximum hardness. We may thus legitimately infer that in the true colloidal range, the surface energy of the highly dispersed Fe_3C must play an important part in the hardening of

* At the time Jeffries and Archer proposed their theory (1921) we had just begun to use the X-ray spectrometer in metallurgical work. The X-ray spectrograms of martensite shows broadening of the diffraction lines, which these investigators, following the lead of Debye and Scherrer, interpreted as refinement of the ferrite grains.

† The slip-interference theory requires also that the dispersed phase must be considerably harder than the matrix. This is merely incidental, as compounds, as indicated by their hardness, have high surface energy.

‡ For example, pearlite may be considered loosely as a structural phase, yet from the standpoint of the phase rule, it is composed of two phases, ferrite and Fe_3C.

§ The *meta*-martensite may be identical with Honda's α-martensite, in which the ferrite has a body-centered tetragonal lattice. We must not overlook the fact that the extremely fine particle-size of the Fe_3C stable in the low-temperature tempering range, would result in the ferrite being supersaturated. This hardened ferrite will, of course, contribute towards the total hardness of martensite. The point of maximum hardness can then be defined mathematically as the point at which the algebraic sum of the hardness of the supersaturated ferrite and the total effective surface energy of the dispersed Fe_3C, is at a maximum.

steels. The writer, therefore, suggests for consideration the rôle of surface energy in the phenomenon of precipitation hardening of alloys.

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The Properties of Thin Films on Metals

By Ulick R. Evans, Cambridge, England.

Metallic silver exposed to iodine vapor or immersed in iodine solution becomes converted superficially to iodide,[1] and the film very rapidly passes through the range of thicknesses needed to yield interference tints; the thickening is rapid at first, but gradually slows down since the iodine has to diffuse through a continually increased depth of iodide to reach the metal. Similarly copper exposed to air containing hydrogen sulfide develops interference colors due to copper sulfide. In both cases, the tints appear at ordinary temperatures, indicating that diffusion can occur quite readily at these temperatures through solid iodides or sulfides. But metals can be exposed to oxygen at ordinary temperatures indefinitely without visible change provided that no moisture condenses on the surface; interference films, due to oxides, only appear when the temperature is raised. Oxide films are actually produced at ordinary temperatures, but since the diffusion through solid oxide at low temperatures is very slow, the films stifle their own growth, and do not reach the thickness needed to produce interference tints. Such films are "invisible" while they remain in optical contact with the metal, but they become visible when isolated from the bright reflecting basis, and are then found to be exactly similar to the oxide films responsible for the tints on heated metal except that they are thinner.

Various methods have been used to isolate the thin oxide films from their metallic basis. In the case of the films responsible for "heat tints" on lead, the author has used a purely mechanical method to lift off the films from the metal, which is a liquid at the temperature in question.[2] When the metal is solid, it is necessary to "undermine" the film by some treatment which will dissolve the metal and leave the oxide. The author [3] has used an iodine solution to isolate oxide films from iron and in this way has studied both the comparatively thick (non-protective) films responsible for heat tints, and also the thinner and more protective "invisible" films responsible for "passivity." He has also used an anodic method for isolating the films from iron, also nickel and copper. Recently this anodic method has been improved by J. Stockdale and the author,[3a] and has been applied to the isolation of oxide films from iron, steel, nickel, copper, stainless steel and other alloys; this improved method will shortly be published. For the isolation of the oxide films from aluminum, it is best to remove the metal as its volatile chloride, by heating in a current of dry hydrogen chloride gas—a method developed by Sutton and Willstrop.[4]

When produced by exposure of metals to air, oxide-films never reach "visible thickness" at ordinary temperatures—as already explained. Nevertheless, oxidation commences very quickly, although it soon slows down; three different groups of workers—using three different methods—have obtained evidence of appreciable oxidation after only a few seconds' exposure to air

at room temperature. Freundlich, Patscheke and Zöcher [5] have reached this conclusion by an optical method; McAulay and Bastow's potentiometric researches [6] point in the same direction, as also do the author's own work on the direct removal of the films.[7]

The thickness of the films responsible for the "temper-colours" (interference tints) on iron have been measured by Constable,[8] who finds that the blue color corresponds to a thickness of 720 Å, the brown-red color to a thickness of 580 Å, and the straw yellow to a thickness of 460 Å. Below about 400 Å, films produce no change in the appearance of iron, although—if sufficiently continuous—they may modify the chemical properties, e.g. the reaction with copper nitrate solution. It is widely believed that the thickness of a film responsible for a given "interference tint" can be obtained simply by dividing the thickness of the "air-film" needed to produce the same thickness by the refractive index of the oxide, and many researches on the velocity of film growth have been based on this convenient assumption. This procedure might yield approximate results in some cases, but optical considerations suggest that the assumption is not in general correct,[9] and it is feared that serious errors will occur, if the method continues to be used. The question, which is clearly of considerable importance in connection with the velocity of reactions leading to films, has been investigated experimentally by L. C. Bannister and the author, and the results show that, for silver iodide films, the method is not accurate.[9a]

The thickness of the "invisible" films responsible for passivity or protection varies greatly with the metal chosen, its surface state and the conditions of oxidation. In general, a highly "protective" oxide will form a thinner film than a less protective oxide; for in the first case, oxygen will be excluded from the metal when a very small thickness has been reached, and thickening will then cease; the film on "stainless steel" is definitely thinner than that on "ordinary steel" heated for the same time at the same temperature. Since a thin film is less likely to crack than a thick film, the practical advantage of using such materials is easily understood; films thick enough to yield interference tints have usually little protective value.

With any given material, the film is likely to be thinnest and most protective if the surface is smooth and free from stresses of a kind likely to crack the film; Freundlich considers that the film present on an iron mirror produced on glass by decomposition of the carbonyl and then exposed to air, is about 10 Å.[10] The surface of iron first abraded with coarse abrasive appears to be pierced with microscopic cracks or fissures; the measurements of Bowden and Rideal [11] have indicated that abrasion produces an enhanced surface area; at all events, abrasion leaves serious internal stresses in the surface layers. Accordingly, with coarsely abraded iron, a longer exposure to air is needed before passivity towards copper nitrate is produced than with finely abraded iron and the protection is more likely to break down; the thickness reached on coarsely abraded iron may approach the values needed for interference tints, and although the first (yellow) interference color is never reached by simple exposure to dry air at ordinary temperatures, yet a yellow color is sometimes produced on steel rendered passive by some weeks' immersion in potassium chromate solution, and even still more quickly on copper treated in the same liquid.

Although films produced on iron by exposure to oxidizing agents (or even, with pure iron, by exposure to air) may prevent attack by copper nitrate solution (a liquid which rapidly attacks freshly abraded iron), they do not prevent corrosion by ordinary waters or salt solutions. With stainless iron or steel,

the film formed gives far better protection. With ordinary steel, satisfactory protection may sometimes be obtained, if the water used is "treated" with chemicals—such as chromates or hydroxides—suited to keep the film in good repair—a method successfully developed by Speller;[12] it should be added, however, that the use of film repairing chemicals may have its limitations and even its dangers if chlorides are present, since these appear capable of piercing the film at places, and sometimes set up local but very intense corrosion.[13] In the absence of special "film-repairing" chemicals, the effect of films on ordinary iron and steel is to cause the attack to set in first at the place where the film is weakest. Such places may be parts where residual stresses (left by cutting or bending) occur in the metal, or where rolling defects, flaws, pores or inclusions occur in the surface. Under some circumstances (only) the water line may constitute a weak place. Jagged edges often constitute weak points; possibly this may be due to the fact that an uncompressed oxide usually requires a greater volume than that occupied by the metal contained in it; thus an oxide film produced by oxidation of a flat metallic surface tends to be in a state of slight compression—a fact which may militate against penetration by ions; but at a jagged point, this state of compression need not exist, and penetration is more likely to occur. However produced, these weak points tend to be anodic towards the part where the film is in better condition, and the attack started often extends, as the secondary corrosion products spread out, shutting off the supply of "repairing oxygen" from the surface around.[14]

In general, the distribution of dissolved oxygen in the liquid is the determining factor in deciding the manner of corrosion. Where oxygen is in excess, the film is kept in good repair, and the metals tend to be cathodic, whilst the parts inaccessible to oxygen—either because they are too far below the liquid surface, or because they are screened from oxygen by a loose secondary corrosion-product (such as the mixture of precipitated iron hydroxides known as "rust") are anodic and suffer attack. Local anodic attack may occur where an otherwise inert substance (such as glass) rests against the surface and shields it from oxygen; the "deposit attack" produced by débris in brass condenser tubes is of this character. In all cases, however, the electric current continues to flow only if oxygen is supplied (as a depolarizer) to the cathodic portion. *Thus oxygen is required for this type of electrochemical corrosion but the attack actually occurs at the parts relatively inaccessible to oxygen.* This apparently paradoxical generalization is commonly known as the "Differential Aeration Principle," and has wide application in corrosion problems. Although closely connected with thin films, it cannot be considered further here; the author has discussed it in some detail elsewhere.[15]

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The Colloids and the Corrosion of Iron *

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Any satisfactory theory of corrosion must be capable of explaining the following fundamental facts:

1. *Iron does not rust in dry air.* The author has many tubes in which pure electrolytic iron foil has been kept for thirteen years in contact with air dried over phosphorus pentoxide, and not one shows the slightest sign of oxidation or tarnish. If, however, the metal is heated in contact with this very dry air, a thin superficial layer of oxide is formed, giving rise to the well-known tempering colors. But this is not rust.

2. *Iron does not rust in pure liquid water* in the entire absence of air. Pure Swedish iron has been kept by the author for twelve years under these conditions and, apart from the merest trace of tarnishing, which could only be detected under a bright light, there was no apparent change. Even at its boiling point water has no action on the compact metal, although the finely divided metal decomposes it with evolution of hydrogen.

3. *Iron does not rust in moist air at constant temperature,* provided no liquid water condenses on its surface. It is when the temperature fluctuates below the dew point that corrosion takes place.[1] In other words, *liquid water is essential to corrosion.* This finally disposes of the idea that corrosion is a simple case of direct oxidation.

Of the various theories advanced to account for the corrosion of iron, two only of the early ones call for consideration here. Of these, the older is the so-called *acid theory* which was summarized by Calvert [2] in 1871, according to which water and air alone cannot induce the corrosion of iron. An acid substance must also be present to enable the iron first to pass into solution. Since in most cases of natural corrosion carbonic acid is one of the chief accelerators of the reaction, the changes taking place may be represented by the following equations:

$$(1)\quad Fe + 2CO_2 + 2H_2O = \underset{\text{Soluble ferrous bicarbonate.}}{FeH_2(CO_3)_2} + 2H$$

$$(2)\quad FeH_2(CO_3)_2 + Aq. = FeO.Aq. + H_2O + 2CO_2$$

$$(3)\quad 4FeO.Aq. + O_2 = \underset{\text{Rust.}}{2Fe_2O_3Aq.}$$

The nascent hydrogen liberated in accordance with equation (1) combines with dissolved oxygen to form water. The carbon dioxide liberated by the hydrolytic decomposition of ferrous bicarbonate, as shown in equation (2), is free to attack more iron. Thus a small quantity of acid is able to assist catalytically in the oxidation of an indefinite quantity of metal. This theory has frequently been termed the *carbonic acid theory of corrosion,* but such a

* By courtesy of The Iron & Steel Institute, from whose Journal much of this paper has been taken.

term is too restricted, for almost any acid is capable of acting in the above manner. Neither is it essential that the acid should be free, for neutral salts, such as sodium chloride, even when rendered faintly alkaline, readily stimulate corrosion. In other words, according to modern views, small quantities of an electrolyte are assumed to be necessary to induce corrosion.

In 1903, Whitney [3] suggested a somewhat different explanation, according to which, water being an electrolyte and therefore split up to a small extent into hydrogen and hydroxyl ions, it is unnecessary to postulate the existence of a catalyst before corrosion can take place.

Thus, the condition of equilibrium between liquid water and its ions may be represented by the scheme:

$$nH_2O \rightleftharpoons (n-1)H_2O + H^{\cdot} + OH'$$

On placing iron in the water, some of the metal passes into solution in the ionic condition, an equivalent amount of hydrogen being liberated on the surface of the undissolved metal. Thus:

$$Fe + 2H^{\cdot} + 2OH' \rightleftharpoons Fe^{\cdot\cdot} + H_2 + 2OH'$$

Admission of oxygen to the system removes the liberated hydrogen by converting it into water, so that increasing quantities of iron pass into solution until saturation is reached, when hydrated ferrous oxide, more or less oxidized by excess of air to the ferric condition, precipitates out.

According to this theory, therefore, pure liquid water and oxygen are alone sufficient to cause the formation of rust.

At first sight it would appear very easy to decide between the two theories, but in practice it is found to be extremely difficult, owing to the elaborate precautions that must be taken to ensure the purity of the materials.

The former theory has received strong support from the researches of Moody [4] and others,[5] and also is in perfect accord with the well-known fact that, as the methods of preparing pure substances become increasingly refined, the number of reactions known to occur between impure reagents but not between them when exceedingly pure, steadily grows.

Whitney's theory is frequently termed the "electrolytic" theory of corrosion. This is distinctly misleading and has led to much confusion because, by implication, the former theory is not to be regarded as electrolytic. In point of fact, both theories will bear equally well the electrolytic interpretation.

The difference, however, is mainly one of academic rather than of technical interest, since absolutely pure air, water, and metal are practically unobtainable. Consequently iron invariably rusts in contact with air and liquid water.

Although thoroughly sound in so far as they go, neither of the foregoing theories is adequate to explain all the phenomena of ferrous corrosion. The modern view, which is essentially a development of Whitney's electrolytic theory, is based upon the observation of Aston * that areas covered by wet rust become anodic to the surrounding metal because of the limitation imposed upon the supply of oxygen, the rust acting as a kind of screen or diaphragm retarding the free access of the gas. This *anodic theory* of corrosion has been largely applied by Evans † to explain the results of his own researches on the corrosion of metals generally, and affords a beautiful explanation for the frequent occurrence of certain types of that most dreaded form of localized corrosion known as *pitting.*

* Aston, *Trans. Am. Electrochem. Soc.*, 29, 449 (1916).

† *See* U. R. Evans, "Corrosion of Metals," (London, E. Arnold & Co., 1926); (*also* his paper in this volume. J. A.).

In 1910 Heyn and Bauer [6] called attention to the fact that if iron is allowed to corrode in moving water, the rate of corrosion at first rises rapidly with the rate of flow. A maximum is soon reached, however, after which further increase in the rate of flow causes the corrosion to decline. The method of experiment consisted in suspending sets of two mild steel plates in beakers, each of 600 cc. capacity, and through which uniform streams of water were continuously maintained for a period of three weeks, from glass delivery tubes connected with the water supply of the laboratory. The rates of flow of the water were expressed as liters per hour, but from the dimensions of the apparatus it is possible to calculate the approximate rates of flow of the water over the surfaces of the plates. The results are as follows:

Velocity of water—				
(1) Liters per hour..........	0	15	50	350
(2) Feet per hour............	0	11	36	250
Relative corrosion [7]	100	240	146	67

Experiments carried out with cast-iron plates yielded analogous results.[8] The method, however, does not admit of the attainment of very high velocities, the maximum reached by Heyn and Bauer being only 250 feet per hour.

In order to determine whether or not it might be possible to inhibit the corrosion of iron altogether at higher speeds, strips of Kahlbaum's electrolytic iron foil were held in wide glass tubes by means of platinum wire, and connected directly to the water-mains, as shown in Figure 1.

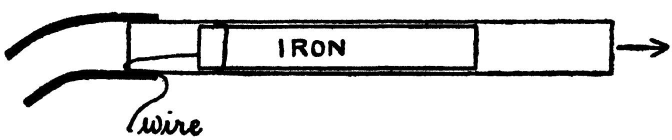


FIG. 1.

By this method the water could be made to flow over the surface of the metal at any velocity up to about six miles per hour. The results were as follows:

TABLE I.

Velocity of Water		Loss in Weight of Iron. Mg. per Hour	Relative Corrosion	Remarks
Feet/Hour	Miles per Hour			
0	0	0.082	100	Rust
540	0.1	0.188	229	Rust
570	0.1	0.177	216	Rust
4,200	0.8	0.054	66	Rust
9,000	1.8	0.029	35	Traces of rust
13,000	2.3	0.032	39	Traces of rust
30,000	5.8	0.045	55	No corrosion

These results are shown graphically in Figure 2. On increasing the rate of flow of the water, corrosion at first increases, then falls to a minimum at a velocity of about two miles per hour, and finally very slowly increases. This latter increase is probably due to mechanical erosion, for no trace of rust is visible.

In order to be sure that lack of aeration of the water was not the cause of the reduced corrosion, the experiments were varied by introducing a side tube between the metal and the main water supply, into which air was sucked as the water flowed through the tube. The surface of the metal was then swept by water, rendered milky with minute bubbles of air. The results, however, were substantially the same.

In order to confirm these remarkable observations, the author requested his friend, Dr. Hatfield, to repeat the experiments with Sheffield water. This was particularly desirable in view of the fact that the experiments described above were carried out with Worcester City tap water, which is known to contain an abnormal quantity of dissolved salts on account of the proximity

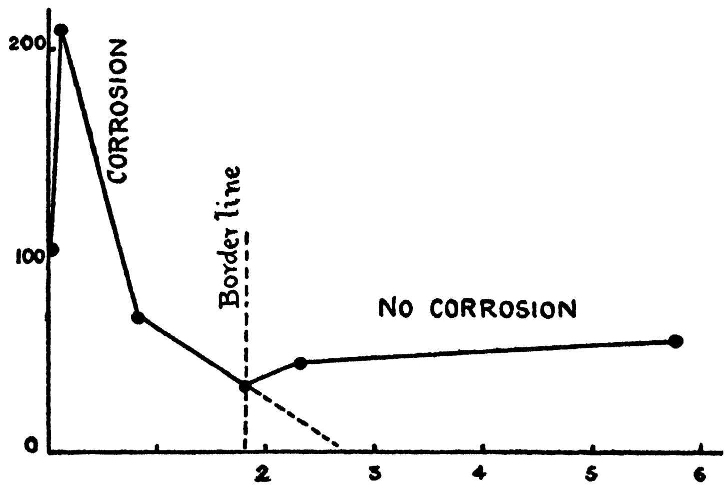


Fig. 2.

of the Severn to the Droitwich salt springs. The experiments could not be repeated with distilled water on account of the immense volume required.

Dr. Hatfield's report was as follows:

"The samples of foil were polished to 000 emery-paper and suspended by platinum wire in a glass tube of suitable diameter, as suggested. The period of test was 48 hours in each case. The temperature of the water was constant at 8° C. during the whole test.

"In the test with water at high velocity the rate of flow varied with a minimum of 2.02 miles per hour (during the day) to a maximum of 5.17 miles per hour(during the night). In the test with water at low velocity the rate of flow varied from one-tenth to one-eighth mile per hour."

The following data were obtained:

1. Water at high velocity—
   No rust formed.
   Loss in weight—14 mg. per square dm.
2. Water at low velocity—
   Definite rusting.
   Loss in weight—109 mg. per square dm.

These results entirely confirm those of the present author. It was thought desirable next to determine whether or not the same retardation is manifested in acid solution.

Experiments to this end were undertaken by Mr. J. H. Dennett, B.Sc., in conjunction with the author. The method consisted [9] in attaching a disc of pure iron foil to a bronze axle, contact between the two metals being prevented by rubber washers. The axle was made to rotate at varying speeds, its lower end, carrying the iron disc, being immersed in a glass tank containing a liter of dilute sulfuric acid. The internal walls of the tank possessed raised vertical ribs, which greatly reduced the tendency of the liquid to swirl round with the

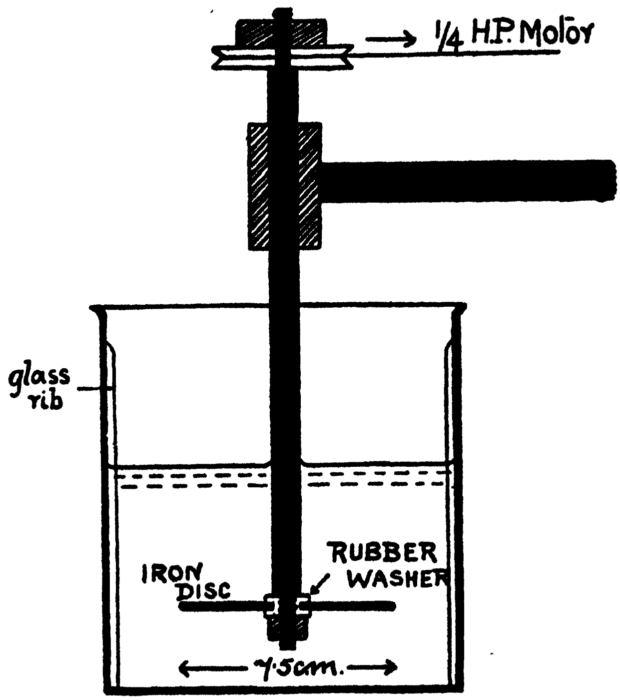


Fig. 3.

rotating disc. The amount of iron dissolved was determined by titration with permanganate. The same disc of iron was used throughout the research in order to avoid fluctuations due to chemical and physical variations characteristic of different samples of the metal. The driving power was obtained from a one-fourth horse-power electric motor, a maximum velocity of 4,000 r.p.m. being reached. The arrangement is shown in Fig. 3, and the results, which are given in Table II, are shown graphically in Fig. 4 for the 0.5 per cent acid.

It will be observed that:

1. The different concentrations of acid yield almost identical results at the same velocities.
2. The rate of solution is directly proportional—within the error of experiment—to the velocity of rotation. Even at 4,000 revolutions, corresponding with a rim velocity of 35 miles per hour, there is no sign of falling off in the rate of solution. Evidently, therefore, solution of iron in acid is a different process from the corrosion of iron in aerated water. In the latter case, corrosion ceases at a velocity of three to five miles per hour, as has been seen.

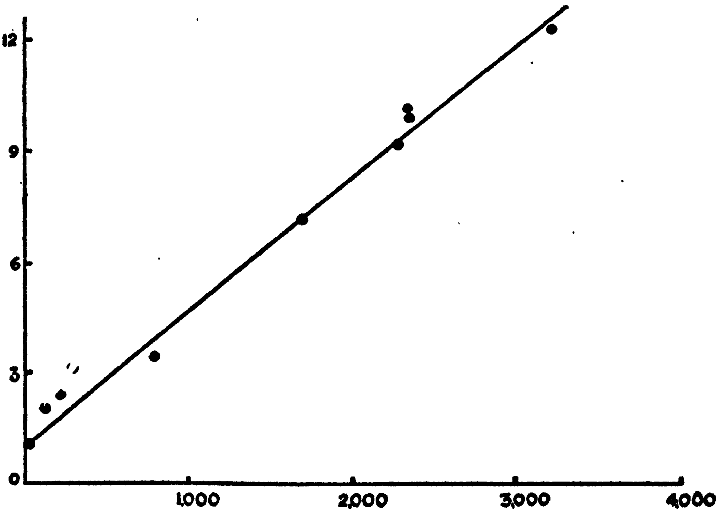


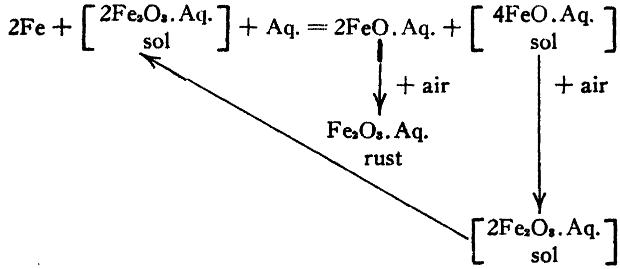
FIG. 4.

TABLE II.

Conc. of H_2SO_4 Per Cent	Temperature	Revolutions per Minute	Relative Rates of Solution
1.0	12.2	2400	10.24
	13.6	3200	12.38
0.5	10.2	0	1.00
	10.0	145	2.11
	9.4	238	2.46
	14.0	300	3.17
	9.8	800	3.32
	13.8	1700	7.62
	12.2	2270	9.18
	12.2	2400	10.24
	12.2	2400	10.00
	13.1	3200	12.24
	14.9	4000	16.90
0.1	9.6	238	2.13
	9.4	238	2.10
	14.0	800	2.95
	13.8	1700	7.47
	12.2	2400	10.00
0.05	13.2	800	3.06
	13.8	1700	7.13

These results have been extended by Whitman and his coworkers.[10] There is thus a great difference between corrosion in more or less neutral solution and corrosion which is the result of acid attack, in which the products of corrosion are soluble and readily wash or diffuse away from the seat of attack. The present author, therefore, suggested [11] that pure iron is relatively noble or passive to pure water and only passes very slowly into solution in oxy-

genated water in the absence of a catalyst. The dissolved iron is probably present at first in solution in the more or less completely ionized condition and it was suggested that agglomeration of ferrous hydroxide to the colloid state probably takes place, the sol or gel thus formed catalytically assisting the as yet unattacked metal to undergo oxidation. At first the *modus operandi* of the colloid was believed to be chemical, the sol or gel being alternately reduced and re-oxidized in contact with the iron and air respectively. Thus:



Such reactions are theoretically possible, and agree with the well-known catalytic activity of iron and its salts in numerous reactions. But a series of carefully planned experiments designed by the author to test this theory have yielded negative results. Whilst, therefore, the foregoing scheme is still possible, it appears more probable that the action of the colloid is simply mechanical. That is to say, in rapidly moving aerated water the iron passes very slowly into solution and the ions are swept away. Under stationary or slow-moving conditions the iron passes into solution, the ferrous hydroxide agglomerates to sol or gel and is adsorbed on to, or otherwise clings to, portions of the metallic surface, thus partially screening them from oxygen and inducing anodic corrosion in accordance with recognized electrochemical principles.

The corrosion of iron under such conditions is therefore largely interwoven with colloid phenomena, for it is evident that any reaction or process that will retard adsorption of the colloid, and hence the screening of the metallic surface, will tend also to retard anodic reactions.

Influence of Dissolved Salts upon Corrosion.

As a general rule, if a small quantity of an inorganic salt is dissolved in water in which iron is corroding, the rate of corrosion is enhanced. The rate increases with the salt concentration until a maximum is reached, termed the *critical concentration.*[12] Further concentration of the salt reduces the corrosion, which may ultimately fall to nil, at what is termed the *limiting concentration.*[12] In the majority of cases the solution becomes saturated with the salt long before the limiting concentration is reached. This latter therefore becomes a hypothetical number, as, for example, in the case of the chlorides and sulfates referred to in Figure 7.

The fall in corrosion in the case of saturated solutions of sodium chloride (brine) was explained by Adie[13] as being the direct result of the reduced solubility of oxygen in the solution, for, as has since been shown,[14] the rate of corrosion is directly proportional to the concentration of dissolved oxygen. Now while this is undoubtedly an important factor, it cannot be the only one, in as much as experiment shows that the reduction in corrosion is usually very much greater than the above theory demands. Such was found to be the case,

for example, with potassium sulfate solutions at 15° C., as is evident from the following data:

Concentration of K_2SO_4 (grams per liter)	0	5	10	15	50	100
Relative corrosion[15]	100	70	115	120	23	14
Relative oxygen solubility[16]	100	97	94	91	80	65

These results are shown in Figure 5, and it will be evident that if Adie's explanations were complete, the corrosion curve should show a general similarity to the oxygen solubility curve. This is clearly not the case, for whilst the corrosion in the 100 gram solution has fallen from 100 to 14, the oxygen solubility has only fallen to 65.

On the other hand, experiments with sodium chloride solutions[15] at 23.5° C. yielded results agreeing quite well with Adie's theory. Thus:

Grams NaCl per liter....	0	5	10	15	30	60	120
Relative corrosion	100	91	94	95	81	76	60
Relative oxygen solubility	100	97	94	91	84	74	50

A glance at Figure 6 suffices to show the close similarity between the corrosion and solubility curves.

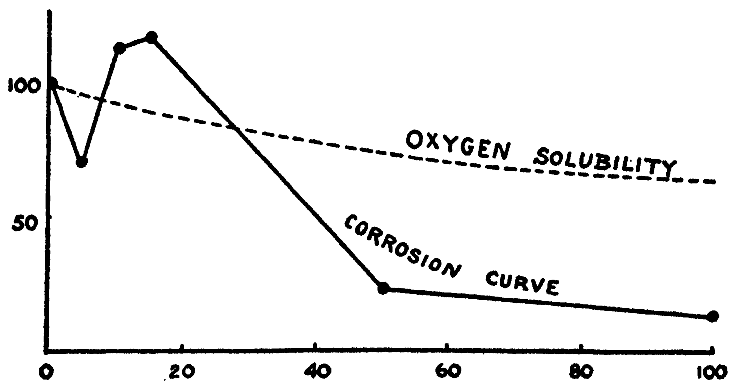


FIG. 5.

For many years it has been known that acid radicles, which are electronegative in character, possess a powerful precipitating action upon positive colloids, such as the sols of iron hydroxide now under consideration. It is only to be expected therefore that addition of salts to water in which iron is corroding will exert a triple effect, namely: (1) Accentuate the rate of solution of the iron by ionic activity. This explains the rise in the curve to the maximum or "critical" point; (2) when the salt concentration is sufficiently great to exert a precipitating action upon the colloidal iron hydroxide, adsorption and hence anodic attack will be reduced; (3) at high concentrations, also, the reduced solubility of the oxygen will tend to retard corrosion.

The actual extent of corrosion, therefore, at any special salt concentration is the result of the algebraic sum of the above factors.

Now if the above explanation is correct, it is evident that a definite similarity should be traceable between the influence of salts upon corrosion and their effect upon sols of iron hydroxide. Such is the case.

Numerous investigators have studied the precipitating effect of certain

salts upon colloidal ferric hydroxide, and all agree that smaller quantities of bivalent anions (*e.g.* sulfates) are required than of univalent anions (*e.g.* chlorides) to precipitate their sols. The order of precipitation, as found by Linder and Picton,[17] is as follows:

	Relative Precipitating Power
Chromates and dichromates	1,000
Sulfates	670
Chlorides and nitrates (about equal)	3

In other words, while very small quantities of chromates and bichromates will precipitate colloidal ferric hydroxide, large quantities of chlorides are essential, in view of their feeble coagulating powers. Sulphates lie intermediately.

It is therefore to be expected that small quantities of chromates and bichromates will serve to inhibit corrosion; large quantities of chlorides will be required to produce similar effects, and intermediate concentrations of sulfates.

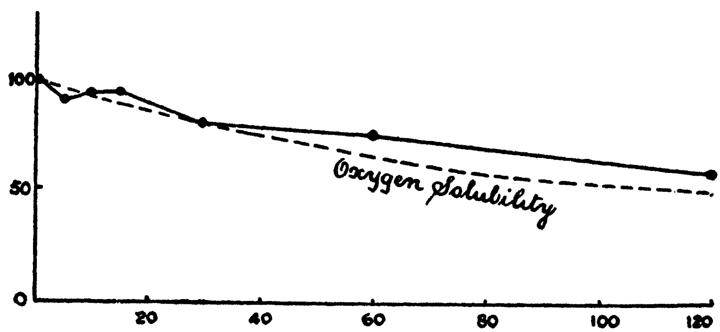


FIG. 6.

That such is the case is abundantly evident from a consideration of the data in Table III, and shown in the form of curves in Figure 7, in which the concentrations of the salts are expressed in terms of the acid radicle or gram-anions per liter,[18] and the corrosion of iron in distilled water is taken throughout as 100, all other corrosions being expressed relatively thereto.

It is now clear why the oxygen solubility curve in Figure 5 differs from the corrosion curve, for the precipitating action of the potassium sulfate is superimposed upon the retarding effect of reduced oxygen solubility. In the case of sodium chloride, however, the precipitating action of this salt is relatively small, so that the corrosion curve is not so far removed from the oxygen-solubility curve in Figure 6.

The nature of the metal or positive ion undoubtedly exerts an influence too, although less important than that of the acid radicle or negative ion. For example, Hardy[19] found that the concentration of barium chloride required to precipitate ferric hydroxide sol lies intermediately between that of sodium chloride and potassium sulfate. The curves in Figure 7 show in a very striking manner a similar parallelism.

Influence of Temperature upon Corrosion.[20]

Colloidal ferric hydroxide is so stable that the pure suspensoid in water may be boiled without precipitation. If small quantities of a salt are added,

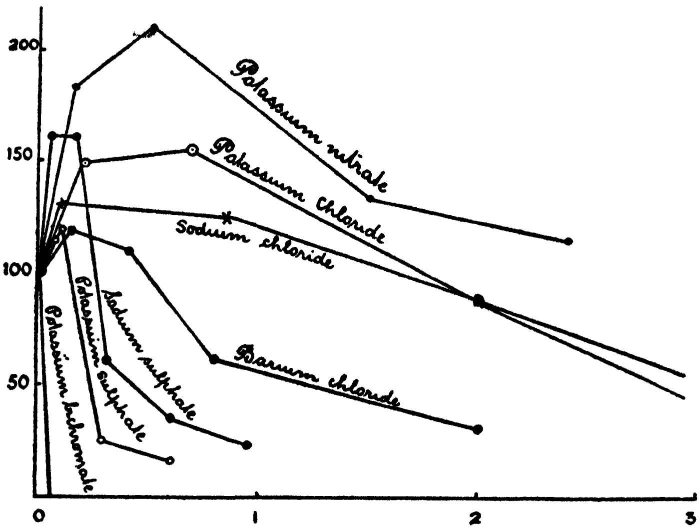


FIG. 7.

however, precipitation readily takes place. It is to be expected, therefore, that the rate of corrosion of iron will rise rapidly with the temperature in common with all exothermic reactions and, in the case of completely submerged specimens, where fairly pure water alone is the liquid phase, the point

TABLE III.

Potassium Nitrate, 13.5° C.			Potassium Chloride, 15° C.			Potassium Sulfate, 15° C.		
Grams KNO_3 per Liter	Gram-Anions per Liter	Relative Corrosion	Grams KCl per Liter	Gram-Anions per Liter	Relative Corrosion	Grams K_2SO_4 per Liter	Gram-Anions per Liter	Relative Corrosion
0	0	100	0	0	100	0	0	100
15	0.15	183	15	0.2	149	5	0.03	70
50	0.50	210	50	0.67	155	10	0.06	115
150	1.50	133	150	2.0	88	15	0.09	120
240	2.40	114	300	4.0	16	50	0.29	23
						100	0.58	14
Sodium Chloride, 16° C.			**Sodium Sulfate, 15° C.**			**Barium Chloride, 15° C.**		
Grams NaCl per Liter	Gram-Anions per Liter	Relative Corrosion	Grams $Na_2SO_4 \cdot 10H_2O$ per Liter	Gram-Anions per Liter	Relative Corrosion	Grams $BaCl_2 \cdot 2H_2O$ per Liter	Gram-Anions per Liter	Relative Corrosion
0	0	100	0	0	100	0	0	100
1	0.02	104	5	0.02	112	5	0.04	111
5	0.09	130	15	0.05	163	15	0.12	121
50	0.85	124	50	0.16	161	50	0.41	111
120	2.04	89	100	0.32	59	100	0.82	62
200	3.40	42	200	0.63	35	250	2.05	30
360	6.12	8	300	0.95	23			

Very small quantities of potassium bichromate entirely inhibit corrosion.

of maximum corrosion will be almost entirely dependent upon the ease with which oxygen can gain access to the metal. This latter is largely a function of the solubility of the gas. Experiments agree with this expectation, the point of maximum corrosion occurring, under the conditions of the experiment, at about 80° C., the rate of corrosion being then more than seven times as great as that at 0° C.

In the presence of dissolved salts, however, the reactions are more complicated. Owing to the enhanced precipitating action of salts with rise of temperature, their critical concentrations fall, and relatively to water at the corresponding temperatures the corrosive action of the solutions also falls.

The steady fall of the critical concentrations is well illustrated by the following data:

Salt	Temperature, °C.	Critical Concentration Grams/Liter
Barium chloride ($BaCl_2.2H_2O$)	6	50
	12	50
	15	15
	18	5
	24	5
Potassium chloride (KCl)	3.5	50
	10	50
	15	15
	18	15
	23	5
Potassium nitrate (KNO_3)	5	50
	9.5	50
	13.5	15
	18	1
	23	1

Action of Alcohol.

The action of alcohol on iron is interesting in view of the use of steel tuns as containers. Up to the present experiments have only included mixtures of water and pure ethyl alcohol. If the oxygen solubility in the mixtures were the only factor, or even the most important one to be considered, the corrosion curve should follow the solubility curve. As shown in Figure 8, however, this is not the case. The solubility curve (broken line) falls to a minimum and then rises rapidly. It is drawn to half scale in the diagram for convenience of representation. The corrosion curve (continuous line), on the other hand, rapidly falls, until with absolute alcohol corrosion ceases.

Action of Poisons.

It is well known that catalyzed reactions may be hindered or even stopped by the addition of small quantities of certain substances, which are termed "poisons." The poison appears to attack, or be superficially adsorbed by, the catalyst, which is thereby rendered inert. Most of these poisons are actually poisonous to the animal system, whence their name.

Now colloidal ferric hydroxide readily adsorbs arsenious oxide, and has been recommended as an antidote in cases of arsenical poisoning for that

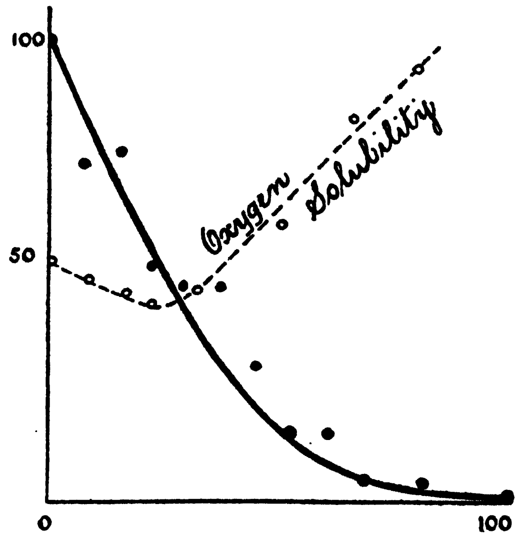


FIG. 8.

reason. It is most suggestive, therefore, to find that arsenious oxide is a powerful inhibitor of corrosion.[21] Sodium arsenite behaves similarly, and the custom of adding this to boiler feed-waters to reduce corrosion [22] is well known.

Action of Radium Rays.

Were the corrosion of iron a purely ionic effect, exposure to radium rays should lead to an acceleration of corrosion, for it is well known that oxidation processes are usually very sensitive in this respect. On the other hand, radium rays tend to precipitate iron hydroxide sol and exposure to radium should retard corrosion.

Experiments were arranged to test this. A small metal capsule containing 0.1 milligram of radium chloride was suspended above a shallow earthenware dish containing a disc of pure electrolytic iron foil, as shown in Figure 9.

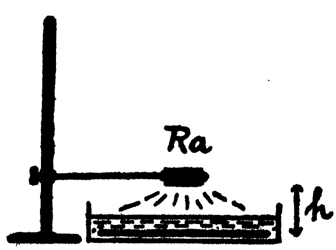


FIG. 9.

The experiment was repeated several times, the height, *h*, being varied, and blanks were simultaneously run. The results clearly indicated a decided retardation of corrosion, despite the extremely feeble source of rays. Thus:

Height, *h* (centimeters)	∞	13	4
Relative corrosion	100	87	85

Influence of Protective Colloids.

The influence of protective colloids has been made the subject of considerable study, and the results are of importance. Protective colloids are usually organic in character, glue and starch being typical examples. The author has shown that dilute solutions of these tend to retard the corrosion of iron immersed in them.[23] The following results were obtained by exposing plates of Kahlbaum's electrolytic iron foil to the action of dilute solutions (0·2 per cent) of the colloids in water for sixteen days:

	Relative Corrosion
Water	100
Gum arabic (acacia)	63
Potato starch	50
Dextrin	50
Gelatin	50
Egg albumen	28
Agar	10

This retarding action is not confined to the corrosion of iron. It has been found by R. H. Vallance and the author to obtain with other common metals such as lead, zinc, and aluminium. The results are of considerable interest, since in most culinary operations colloidal substances are dealt with which pass into the waters and thus retard the corrosion of the utensils.

The retardation increases with the concentration of the colloid, and corrosion becomes negligibly small when the disperse phase is so concentrated as to yield a jelly or "gel." The explanation appears to lie in *adsorption;*[24] that is, an excessively thin layer of the colloid is attracted to the metallic surface and more or less completely covers it, thus proportionately preserving it from attack. The more concentrated the colloid solution, the more complete the coating, and hence the more efficient the preservation.

Herein lies the explanation for the efficiency of paints made with linseed oil. The oil "sets" to a gel, which is strongly adsorbed by the metallic surface, and which therefore affords a very thorough protection to the same.

An interesting case arises when dissolved salts are present in the waters containing the protective colloids. At first the action of the salts is but small, but as the concentration rises it gradually increases, until, at high concentrations, the protective colloid is "salted out," and the results are the same as if no colloid were present. This is well illustrated by the curves shown in Fig. 10, which represent the relative corrosions of plates of pure iron foil immersed for twelve days in solutions of potassium sulfate of varying concentration at 10° C. The continuous line gives the results in the absence of a protective colloid, while the broken line gives those obtained in the presence of 1 per cent gum acacia. At a salt concentration of 60 grams per liter the colloid has been practically salted out, and the two curves meet. The numerical data are as follows:

Grams K_2SO_4 per liter	0	1	5	10	15	25	60
Relative corrosion—							
(1) Aqueous solution	100	100	119	109	151	158	85
(2) Acacia solution	47	57	81	94	76	86	81

It will be observed that the fall in corrosion in the case of the non-colloid solution at a concentration of 10 grams of potassium sulfate is reflected in the acacia solution at 15 grams concentration.

In the majority of cases of corrosion in practice such high concentrations

of salts as are necessary to salt out the colloid do not usually occur, and colloidal matter may with advantage be added to waters to inhibit corrosion provided the colloids are of such a nature as not to chemically decompose in service yielding corrosive products. Thus fatty oils should not be used in

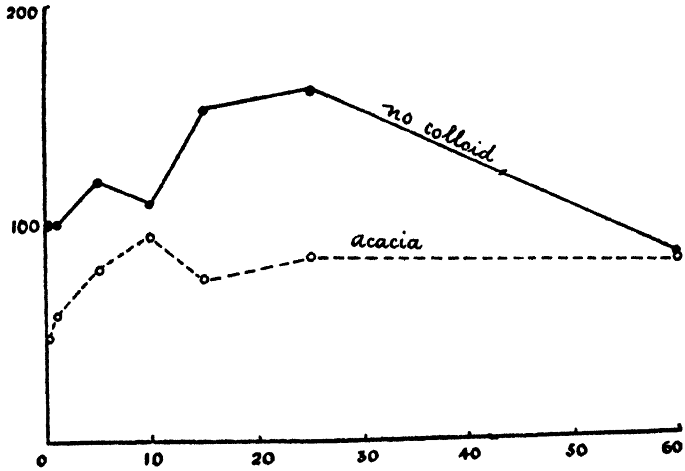


FIG. 10.

boiler practice, as these yield corrosive acids under working conditions. But the practice of boiling bones in an iron boiler before the latter is actually connected up for service has much to recommend it, since the gluey colloids which dissolve out into the water are adsorbed by the metal and tend to protect it from corrosion.

CONCLUSION.

The corrosion of iron is intimately interwoven with colloid phenomena and a careful study of these latter is essential to a thorough understanding of corrosion problems.

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Colloid Chemistry of Petroleum

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A considerable body of evidence is available concerning the colloidal nature of crude petroleum and some of its distillates. Crude oil of the paraffin-base type (i.e., oil which on distillation yields solid paraffins in the high boiling fractions) usually contains colloidal amorphous matter which only assumes the crystalline state after distillation. It is probable that the effect of heat in this case is physical, bringing about a change of state whereby the wax is no longer in the dispersed condition characteristic of the original oil, although at the same time there is ample evidence to show that the vaseline-like amorphous matter has a higher molecular weight than the crystalline paraffins which result from the distillation of this material.

Thus Cheseborough vaseline has a molecular weight of 646 and a mean composition approximately agreeing with this formula $C_{45}H_{90}(C_nH_{2n})$, whilst wax of 105° F.M.P. possesses a much lower molecular weight (362) and a paraffinoid formulation of the mean value $C_{26}H_{54}$.[1]

Such oils and their residues after the removal of gasoline and kerosene are frequently highly viscous, particularly at low temperatures, owing to the "setting" of the paraffin sol. This phenomenon may be demonstrated by immersion of a suitable residual oil in ice for several hours when the mass appears to be quite solid. A sudden jerk or violent shaking will destroy the quasi solid mass and a thick clotted semi-fluid material will be formed.

The black or dark-colored "asphaltic base" oils contain bituminous matter which is to be regarded as being derived from the petroleum hydrocarbons by oxidation and condensation.

These oils are optically heterogeneous, although in most cases the degree of dispersion is very high[2] (*see* Holde, *Kolloid-Z.*, **3**, 270 (1908); Schneider and Just, *Z. wiss. Mikroskop.*, **22**, 561 (1905).

The colloidal asphaltic material may readily be coagulated by means of strong sulfuric acid.[3] The chemistry of the well-known "acid treatment" has been investigated by B. T. Brooks and I. Humphrey,[4] who showed that the usually accepted view that olefines are polymerized to tar and removed as sludge is erroneous, for pure olefines (up to the C_{16} member) do not give tars with acid, even 100 per cent strength, at 15° C. The formation of "acid tar" is probably a dual phenomenon; firstly, the acid coagulates the colloidal matter present in the oil, and secondly, it brings about polymerization of olefines and diolefines, sulfonation of aromatic derivatives and oxidation of both primary materials and products.

Pyhälä[5] considers that crude oils are sols, of which the disperse phases are solid gels such as asphalt, together with liquid particles. Separation may be achieved by means of centrifuging or the addition of electrolytes. When the disperse phase exceeds 60 per cent the phenomenon of gelatinization makes its appearance.

In an investigation on the viscosity of Mexican oil,[6] it was found that considerable discrepancies in the viscosity occurred between results taken under apparently similar conditions. These differences were much greater than could be accounted for by experimental error, so that it was desirable that the matter should be further investigated. Repeated observations on any one sample gave results which agreed closely among themselves, but if the tests were repeated after an interval of a day or two a different set of values was obtained.

A continuous change appears to be going on in the constitution of the oil, possibly an "association" of molecules to form new molecules of heavier molecular weight. This change is dependent on time and is, furthermore, a function of the temperature to which the oil is subjected. Some of the experimental evidence of this dependence of viscosity and, by inference, of constitution, upon both time and temperature will now be given.

(1) A sample of oil was divided into two portions and was placed in stoppered bottles. The first of these was stored in an ice-safe for six days, while the second was kept for the same period in a hot room at a practically constant temperature of 93° F. The two oils were then removed and the viscosity at 60° F. determined in each case. That stored at 32° F. had increased by 20 per cent of its original value at 60° F., while that maintained at 93° F. had similarly decreased by about 11 per cent.

(2) The effect of increasing the time of exposure to the low temperature was next ascertained and a sample was stored for 120 days; at the end of this time the viscosity at 60° F. had risen to over 2¼ times the original value.

(3) Another sample was heated to about 150° F. for roughly 40 hours, extended over a period of some 10 days; the viscosity at the end of this time was reduced to about half the initial value.

(4) The oil referred to (2) above, which had been kept at 32° F. for a period of 120 days, was divided into several portions; these were heated to a temperature of 100° F. for various lengths of time and their viscosities at 60° F. determined. The high value above noted was rapidly reduced and exposure to 100° F. for about two hours was found to reduce the value to the original figure. Prolonged heating at a still higher temperature would probably have reduced the viscosity still further in accordance with the result noted in (3).

(5) A possible explanation of the above observations would have resulted from the presence of minute solid particles in suspension in the oil, and a test was accordingly made to ascertain whether such particles were present. Some of the oil under consideration was allowed to stand for a period of 34 days in a tall vessel at room temperature (this varied between 45° and 60° F.). Under these conditions it is probable that any solid matter in suspension in the oil would separate to some extent. Samples taken from the top and bottom levels of the oil showed no appreciable difference in viscosity. Tests were at the same time made to trace corresponding changes in density; such changes if they existed were so small as to remain undetected.

The conclusion to be drawn from these investigations is that Mexican oil is subject to a change in viscosity with time: the change is in the nature of an increase if the oil is kept at a low temperature but the normal value may be again obtained by exposure to a high temperature for a comparatively short period. The practical bearing of this is apparent and due precautions should be taken in instances where Mexican oil is stored in outside tanks during the winter months or in cold climates. It might further be remarked that the Mexican oil was the only oil investigated by Glazebrook and his colleagues which showed this "hysteresis" phenomenon. The magnitude of the effect may be greatly reduced, in fact it was rendered practically negligible, by adding a low viscosity oil to the Mexican oil; this was shown experimentally in a test carried out on a 10 per cent mixture of Scotch Shale oil with 90 per cent of the Mexican oil.

The series of investigations which form the bulk of the second part of

this paper make it clear that much work remains to be done in connection with the chemistry and physics of those complex hydrocarbons which are the components of fuel-oils, in order that a clearer idea of their constitution may be obtained and the effect described above is one which can only be fully explained when a more exact knowledge of the complex molecular structure of heavy oils is available.

In discussing the work of Glazebrook and his collaborators the writer drew attention to the peculiar hysteresis effect in the viscosity of fuel oils and showed that by a suitable alteration in the previous history of a given oil, wide variations in its viscosity could be effected.

In Figure 1 the curve *A* is that of a residue fuel oil, prepared in the laboratory. In the course of five or ten days it showed the gradually increasing viscosity to which Glazebrook had referred; then the increase ended and a permanent viscosity was obtained, probably due to the fading away of the thermal change caused in the preparation of the oil. The viscosities were all taken at 25° C.

The curve *B*, drawn to the same scale, is that of a rather more viscous oil. The viscosity increased for a time, then the oil was heated to 60° C. for an

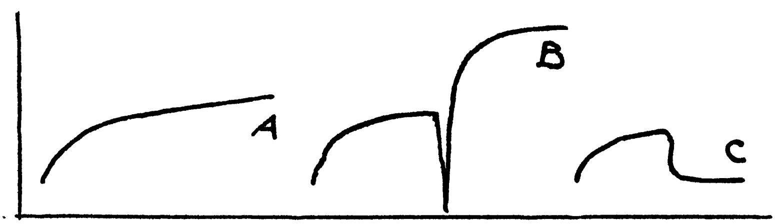

FIG. 1.

hour, causing a fall in viscosity of about 5 per cent; the sample then was immersed in ice for three hours and the viscosity rose accordingly. Two or three days later the hysteresis effect was most effectively shown as the viscosity was still rising slightly.

The third curve is that for an oil, *C*, which after heating for three days and a half recovered its original viscosity. It was then heated for several hours to the temperature of boiling water, and the fall in viscosity showed hysteresis in continuing for some days, after which it slowly returned to the original value.

The corresponding behavior in aqueous gelatin sols affords an interesting parallel. For example, an ordinary jelly can be made by adding water to gelatin in such a way and of such a concentration that the jelly will not set; this jelly is in the sol state. A jelly can also be made so strong that it will set, although, according to domestic information, if heated overlong, setting is inhibited. If, however, this jelly is mashed with a spoon, it becomes liquid or semi-liquid. All those facts observed in connection with jellies can be obtained with certain oils. It is therefore reasonable to suppose that both the phenomena are colloidal.*

The colloidal asphaltic matter in crude oil and the yellow coloring matter in gasoline, kerosene and other distillates which is largely caused by "tar-fog" mechanically carried over, may be removed by coagulation brought about by

* Some of the substance of this chapter was contributed by the author to the Third Report of the Committee on Colloid Chemistry and its general and Industrial Applications. (Dept. of Industrial and Scientific Research, London, 1920.)

agitation with strong sulfuric acid. Direct adsorption on specific surfaces, however, is equally effective. The author has shown that floridin, fuller's earth and bauxite which, when freshly ignited, possess powerful adsorptive properties, follow the well-known exponential adsorption rule $Y/m = ac^{\frac{1}{n}}$. For example when using a 0.25 per cent solution of a crude asphaltic base oil in gasoline as a test liquid, constant values of n were obtained and the $Y/m-c$ curves were of the usual parabolic type.

The application of the adsorptive action of these substances in the refining of various distillates is well known and much of the theoretical side has been admirably expounded by Day and his co-workers.[7]

In brief, these workers have arrived at the following conclusions:

(1) Fuller's earth tends to retain the unsaturated hydrocarbons and sulfur compounds in petroleum, thus exercising a selective action on the oil.

(2) When crude petroleum diffuses upwards through a column of fuller's earth fractionation of the oil occurs. The oil displaced by water from the earth at the top of the tube is lower in density than that from the bottom of the tube.

(3) Furthermore when upward diffusion is employed the aromatic hydrocarbons in a mixture of a paraffin and gasoline tend to collect in the lower end of the diffusion column.

Gilpin and Schneerberger[8] consider that the fuller's earth behaves as a dialyzing septum which allows paraffins and saturated hydrocarbons to pass freely but adsorbs bitumen, aromatic hydrocarbons, sulfur and nitrogen compounds. The determining factor is surface. Similar views are propounded by Gurwitsch,[9] who ascribed Day's results not to capillarity but to specific surface adsorption. This author showed that floridin will adsorb solid paraffin from solution in petroleum ether and benzol but not from lubricating oil. An interesting observation was also made by Herr,[10] who filtered Baku oil through fuller's earth and discovered that all the formolite forming compounds were removed, i.e., the unsaturated compounds which react with formaline were adsorbed on the mineral gel.

It by no means follows that the compounds which are adsorbed can be recovered unchanged. Being possessed almost invariably of residual affinity, the close contact afforded in the adsorbed layer promotes condensation and polymerization, and thus Gurwitsch[11] was able to show that floridin brings about active polymerization when brought into contact with amylene and pinene, resulting in considerable rise in temperature. Curiously enough the same polymer, diamylene, is produced both by sulfuric acid and by fuller's earth. Pinene, similarly, is converted after adsorption into sesqui- and polyterpenes. Alumina behaves in the same way towards amylene but is apparently without effect on pinene. The author's experience has been that freshly ignited precipitated alumina is particularly effective as a decolorizing agent for petroleum and its distillates and a series of experiments using a 0.25 per cent solution of crude asphaltic oil in gasoline showed the following order (see table, top of next page).

The temperature at which the adsorbing surface exerts its specific effect is of considerable importance, as Gilpin and Schneerberger[8] found on passing Californian crude oil through fuller's earth, when, although little fractionating occurred at 20° C., 70° C. gave a satisfactory result.

A peculiar observation made by the writer is of interest in this connection. Cold bauxite, which has been ignited and cooled in a vacuum desiccator was found to have lost its power of adsorbing sulfur derivatives from kerosene. When freshly heated (to 200° C.) its activity in this direction was regained. Heat appears to be evolved during active adsorption, thus a 20° C. rise in

Material (1 gram)	Colored Solution Decolorized cc.
Alumina	60.
Fuller's earth I	30.
Bauxite I	30.
Bauxite II	25.
Bauxite III	20.
Ignited peat	15.
Bone charcoal	14.
Bog iron ore	12.
Fuller's earth II	10.
Ferric oxide	10.
Ball clay	8.
Fuller's earth III	8.5
Fuller's earth IV	4.
China clay	2.
Kieselguhr	2.

temperature was observed during the passage of 100 cc. of kerosene through 50 grams of bauxite.

An extension of this observation proved that the rise in temperature is a direct indication of the activity of the bauxite as a filtering medium, and this property has been employed as a means of testing its value for removal of both color and sulfur compounds from kerosene. Roasted bauxite (50 grams) ready for the filters is poured into a small metal container provided with a thermometer, and crude kerosene (20 cc.) quickly percolated upward through the mass. The temperature rise noted on the thermometer is a delicate indication of the state of efficiency of the material and any deficiency in the roasting or preparation of the bauxite is at once shown up by lack of heat evolution.

Amongst other effective materials may be mentioned Kambara earth,[12] a mineral containing hydrated silica, which decolorizes crude petroleum and adsorbs unsaturated hydrocarbons therefrom. Fibrous alumina has been recommended by Gawolowski,[13] while animal charcoal and prussiate residues have long been employed for these purposes.

Naturally the degree of fineness of the adsorbent is important. The following case will illustrate this point:

Bauxite Mesh	Activity
40/60	1.0
60/80	1.7

In point of fact the activity—all experimental conditions being the same—is approximately directly proportional to the mesh. A convenient method of demonstrating this point consists in treating a 100 cc. of colored solution (e.g. that already mentioned) with varying weights of decolorant, matching the filtered resultant solution with the standard solution in a Nessler jar (C.ccs.) and plotting $\frac{100C}{\text{mass}}$ against C. Ordinates at $C = 50$ give directly the reciprocals of the masses required to remove 50 per cent of the color. Thus with floridin:

Mesh	Mass
Passing 180	50/320
Passing 80 and retained on 180	50/170
Passing 20 and retained on 30	50/44
and with Bauxite	
Passing 80	50/175
Passing 60 and retained on 80	50/80
Passing 20 and retained on 30	50/30

Little can be said as to the relationship between the chemical composition of the material and its adsorbent properties. Apparently hydrated silica or alumina is effective after combined water is expelled but no general statement can be made. Substances giving the same analytical figures may behave quite differently, and again, bodies of dissimilar chemical composition may be equally effective as decolorizing agents.

The essential feature of all effective adsorptive agents is development of surface, hence mineral gels containing water of combination which, on ignition, possess a characteristic structure are decidedly likely to possess decolorizing and desulfurizing properties.

Very characteristic is the behavior of bauxite (say, 40/60 mesh) on being gently agitated with kerosene or gasoline. Apparently a process of peptization goes on, for a considerable amount of very finely divided material separates in suspension in the petroleum which is sufficiently fine to pass readily through filter paper.[14]

The application of bauxite or floridin to refining is very simple. Generally the colored or sulfur-containing distillate is filtered through a column of the adsorbent.[15] The mechanical properties of bauxite and the ease with which it may be granulated render it ideal as a filtering medium. Floridin also may readily be obtained meshed to any required degree of fineness. It is, however, obvious that the adsorbent should be used in a very finely divided state to take advantage of maximum surface and therefore continuous plant such as that used in the application of silica gel is to be regarded as the most useful.

Death Valley clay has been used very successfully but its value is restricted to decolorizing. It possesses little or no selective adsorption towards sulfur derivatives. The adsorbent is applied in the finely divided condition and in the case of lubricating oil vigorous stirring is employed. At almost 150° C. there is evolution of steam and at this point it is likely that the preferential adsorption of color sets in. It has been found in the writer's laboratory that lighter oils may be effectively treated in the cold either by percolation or agitation.

Although in actual refining operations the adsorptive properties of the materials described above have mainly been directed towards the removal of color, yet considerable success has been achieved in connection with the equal important problem of desulfurization. It by no means follows that an adsorbent is equally effective in removing coloring matters and sulfur derivatives. Usually this is not the case, and each material must be tested for its specific purpose. So far as the writer's experience goes, the sulfur compounds present in the lighter distillates are more readily adsorbed than those in the higher boiling fractions, although it is possible that in the latter case, there is preferential adsorption of other substances, e.g., unsaturated hydrocarbons. While, for example, floridin will desulfurize gasoline quite readily, it has little effect on the sulfur compounds which occur in the lubricating oils derived from the same crude petroleum.

An interesting application of adsorption is to be seen in the method patented by Hall Motor Fuel, Ltd., for the purification of cracked gasoline. This material, as is well known, contains a considerable proportion of highly unsaturated hydrocarbons—olefines and diolefines—to the presence of which it owes its characteristic odor and its objectionable propensity towards resinification or "gumming." Although the reactive hydrocarbons can be removed by the agency of strong sulfuric acid the operation is attended by serious loss, but by utilizing the adsorbent capacity of floridin, the diolefines present are polymerized to high-boiling products and a gasoline free from objection is

produced. The refining operation is best carried out with the gasoline by condensation and/or polymerization.

Incidentally the sulfur derivatives present in many gasolines and kerosenes may be removed in a precisely similar manner.

Patrick's work on the adsorptive capacity of silica gel has been developed into a refining method on a commercial scale. An ingenious counter current operation is utilized and the silica gel after successive contact with the oil is re-activated firstly by being steamed and secondly by exposure to heat. The Silica Gel Corporation claim complete desulfurization by this means and have been successful in treating gasoline, kerosene, lubricating oil and cracked gasoline.*

The problem of the breaking of persistent emulsions in refining operations is obviously one for treatment by the application of colloid chemistry. The soda wash which is employed to remove the traces of sulfuric acid in the refining of lubricating oils is a common source of this trouble and sometimes a practically permanent emulsion is formed. The sodium salts of naphthenic and sulfonated naphthenic acids are notable emulsifying agents, and it is possible that herein lies the cause of what is sometimes a serious difficulty. It is interesting to remember that sodium naphthenates are used very extensively as soap.

A recent patent by Southcombe and Wells brings out the novel point that a small amount (1 per cent) of free fatty acid added to a mineral lubricating oil, not only replaces the usual blending fatty oil, but depending on whether its molecular weight is low or high, it yields a non-emulsifying or an emulsifying oil. It appears that the addition of the free fatty acid appreciably lowers the interfacial tension between the lubricating oil and the bearing.

Petroleum jelly or "vaseline" appears to be an emulsion of soft paraffins dispersed in heavy oils. The viscosity increases gradually with decreasing temperature until the gel state is attained, without, however, any separation of crystalline wax, although on distillation, wax appears in the distillate. Various artificial jellies compounded of soft wax and heavy oil are on the market; these are inclined to deposit crystalline matter on being cooled and do not possess the salve-like nature of the natural product.† An apt comparison is in the different appearance of ice cream made with and without the addition of gelatin and in both cases—vaseline and ice cream—the presence of a protective colloid may be the explanation.

Colloidal Fuel.‡

Pulverized coal can now be successfully held in suspension in oil so that the colloidal liquid flows freely through the pipes, pre-heaters and burners of ships and power, heating and industrial plants equipped to burn fuel oil. Months after mixing the composites show little or no deposits. A fixateur, which comprises about 1 per cent or 20 lb. per ton, acts to stabilize the particles of pulverized coal dispersed in the oil. In colloidal fuel every solid particle has its film or liquid hydrocarbon and a protective and peptizing colloid, itself combustible. These particles are in three classes as to dimensions—coarse, colloid and molecular.§ The fixateur and fixed oil are readily made and can be shipped anywhere. The manufacture or distribution of the new fuels

* *See* paper by J. A. Wilson in this volume. J. A.

† By this is meant the material which is obtained from a suitable crude oil by distilling off the lighter compounds and decolorizing the residue (usually by filtration through fuller's earth).

‡ *See* paper by L. W. Bates in this volume. J. A.

§ By coarse is meant the fineness of 50 million particles per cubic inch.

incorporating solid carbon in fixated oils involves no doubtful process or industrial problem. On burning, the combustion is so complete that with fair coal there is left no slag and very little ash; the latter is as light as pumice and granular as sand. It is the property of colloidal fuel that without loss of efficiency per unit volume or change of oil storage or burning equipment it makes possible the conservation of at least 25 per cent of the fuel oil now burned, or conversely with the oils now available it increases by 50 per cent the world supply of fuel that is liquid. We may go further and state that a number of new fuels have been realized, each with varying percentages of oil and solid carbon. One useful composite, in the range of ordinary temperatures, is composed of about half coal and half oil. Another unctuous semi-liquid is nearly three-fourths coal and one-fourth oil. All the fuel pastes are mobile to sustained and easily applied pressure, and may thus be pumped, fed, and atomized in the combustion chamber. These semi-fluid composites will constitute the most compact and safest fuel for domestic and industrial use, and they will largely eliminate the smoke and ash nuisances of cities. For example, industrial colloidal fuel, grade No. 10, devised to use up some poor coal holding 25.5 per cent ash, is composed of 61.5 per cent of pressure still oil, wax tailings, petroleum pitch and fixateur running 18,505 B.t.u. per lb. and 38.5 per cent of "anthracite rice" running 10,900 B.t.u. per lb. This grade contains 162,500 B.t.u. per gallon, and has 10.2 per cent of ash. The fixated oil itself had 151,750 B.t.u. per gallon. In fuel value, therefore, the colloidal fuel of grade No. 10 is worth 7.5 per cent more per gallon than the oil from which it is made. If instead of "anthracite rice" very high in ash, a crude oil coke which is ashless had been employed, the colloidal fuel gallon would have contained 182,154 B.t.u., or roundly, 20 per cent more than the oil base, and 0.25 per cent sulfur.

According to Wm. Ostwald[16] petroleum oil fractions of high boiling point are to be classed as iso-colloids, i.e., a category in which the disperse phase and the dispersion medium possess the same (or analogous) chemical composition.

The ultramicroscopic examination of a number of mineral lubricating oils[1] has demonstrated that optical heterogeneity exists, although, however, the degree of dispersion is exceedingly high. The same behavior obtains for the fatty oils and it is possible that lubricating power is in some way connected with this iso-colloidal state.

Lubricating greases are examples of oil-water emulsions stabilized by soap. Commonly sodium soaps are used for motor greases and the proportions are lubricating oil (sp. gr. 0.900-0.910), 80 parts; stearic acid, 15 parts; and caustic soda, 2 parts. Part of the oil is mixed with the stearic acid and this is added to the soda in 40 per cent aqueous solution, with constant agitation. The remainder of the oil is then incorporated. Cheaper greases are compounded with lime soaps.

Stable petroleum jellies or "solidified petroleum" are made by incorporating petroleum distillates, e.g., kerosene with aqueous soap solutions. The sodium stearate jellies are not very firm and speedily exude oil. Wax may be used to stiffen the jelly. Anhydrous calcium soaps give clear solutions with petroleum oils, gelling on being cooled.

Acheson's oil-dag and aqua-dag are suspensoids of graphite in oil or water containing a protective colloid (tannin). Aqua-dag is made first, and the graphite is transferred from this to oil.* The oil-dag contains about 15 per cent of "deflocculated graphite" and is used in a dilute solution of lubricating

* *See* paper by E. G. Acheson in this volume. J. A.

oil (0.1 per cent graphite) with beneficial results to the bearings, which gradually become coated with a "graphitoid" layer.

The colloidal graphite in oil-dag may be removed for analysis in two ways. Freundlich[17] throws out the graphite by adding an electrolyte (acetic acid) to the benzol solution of the oil-dag, whilst Holde[18] adsorbs the graphite on recently ignited fuller's earth in a Gooch crucible. A German proprietary material named "Kollag" appears to be similar to oil-dag.

The influence of colloidal bituminous matter which is mechanically carried over during distillation is frequently sufficient to prevent the easy separation of paraffin wax from that fraction known as "heavy oil and paraffin," and recourse is made to a sulfuric acid treatment before refrigeration. The paraffin scale is usually discolored and contains a greater or less amount of uncrystallizable material which is removed by the process of "sweating," i.e., fractional fusion. This operation serves to raise the melting point of the wax and also in part to purify it. Final decolorization is effected by filtering the melted wax through fuller's earth, bauxite, or prussiate charcoal.

The following account of the colloidal nature of asphalt is taken from Clifford Richardson's paper in the "Third Report of the Committee on Colloid Chemistry and its General and Industrial Applications" (Dept., Industrial and Scientific Research, London, 1920).

The presence of mineral matter in a high state of subdivision in a system solid-liquid, the matter phase consisting of asphalt reveals some interesting phenomena, connected with the relation of surfaces of solids and films of liquids, particularly where the mineral matter is sufficiently subdivided to exist in a colloidal state as regards the bitumen. Owing to the viscosity of such a continuous phase the particles of mineral matter with which it is associated may be regarded as in a colloidal state, although they may be of dimensions which would prevent their existence in such a state with a more mobile liquid, such as water. Clay and finely divided silica present such a relation to a highly viscous liquid, asphalt for instance, which may be regarded as a colloidal one. Attention was attracted to the subject in the course of a study of the native asphalt found in the Pitch Lake in the Island of Trinidad, British West Indies. This deposit is unique from a geophysical standpoint. It exists in a crater of an old mud spring on the West Coast of the island, and at a distance of about half a mile from the Gulf of Paria. Its surface was originally 138 feet above sea level. Borings which have been recently made show that the crude asphalt exists to a depth of more than 175 feet at the center of the deposit, which consists of a bowl-shaped mass covering, originally, an area of 114 acres. Specimens taken at various points on the surface and at different depths show that it originates in an asphalt petroleum, derived from oil sands occurring at considerable depth below the lake, with which a paste of mineral matter and water, originating in a mud spring, has become associated by the churning action of the natural gas accompanying the petroleum, and the release of the pressure to which it has been subjected as the oil approaches the surface. The material formed in this way is of highly uniform composition in all parts of the deposit, and consists of an emulsion of bitumen with a paste of clay and fine sand, and has the following percentage composition: Bitumen, 39; mineral matter, 27; water and gas, volatile at 100° C., 29; water of hydration of mineral matter, 5.

The water, which on melting the asphalt under certain conditions can be separated therefrom, in a somewhat concentrated condition, has been found to contain in solution large amounts of sodium chloride and sulfate with a considerable amount of ammonium and ferrous sulfates, together with borates

and readily recognizable percentage of iodides. It also contains smaller amounts of potassium, calcium, and magnesium salts. It is plainly of thermal origin.

Refined Asphalt.

As it occurs in the deposit it is known as crude asphalt. As such it is submitted to a process of so-called refining at a temperature of 325° F., which removes the water and results in a material known as refined asphalt, which has the following percentage composition: Bitumen, 57; mineral matter, 39; water of hydration of clay, 4.

In determining the percentage of bitumen in the refined material by means of solvents, it is found that some of the mineral matter passes through the finest filters and is not removed from the solution on prolonged centrifuging. Ultramicroscopic examination shows that the mineral matter of the mud spring which existed in the colloidal state as regards the water with which it is associated, is introduced into the bituminous phase on the removal of the water on refining. The amount of mineral matter in the colloidal state depends on the concentration of the solution, that is to say, upon its viscosity, as shown by the following data:

Table 1.—*Characterization of Solutions of Trinidad Asphalt (T.R.A.).*

Concentration Per Cent	Specific Gravity	Specific Gravity Increase for 1 Per Cent (T.R.A.)	Absolute Viscosity of Solution	Viscosity Difference for 1 Per Cent (T.R.A.)	Refined Colloidal Matter Per Cent	Refined, Amount Calculated per 1 Per Cent (T.R.A.)
Solvent: Benzol	0.876	—	0.00652	—		
1 per cent (T.R.A.)..	0.877	0.0010	0.00654	0.00002	2.54	2.54
2 " " " ..	0.879	0.0020	0.00687	0.00033	2.01	1.00
5 " " " ..	0.883	0.0013	0.00759	0.00024	2.09	0.42
10 " " " ..	0.889	0.0012	0.00961	0.00040	2.73	0.27
20 " " " ..	0.911	0.0022	0.01629	0.00067	3.13	0.16
30 " " " ..	0.930	0.0019	0.04198	0.00257	4.19	0.14
40 " " " ..	0.957	0.0027	0.09477	0.00521	6.51	0.16
50 " " " ..	1.012	0.0055	0.31800	0.02240	10.69	0.21
100 " " " ..	1.400	0.0076	—	—	35.40	0.35

In dilute solution it appears that the amount of matter in a colloidal state is comparatively small, but with increased concentration, that is to say, with increased viscosity of the continuous phase, it becomes progressively larger until in the refined asphalt itself all of the mineral matter, at ordinary temperatures, may be regarded as in a colloidal state. Trinidad asphalt appears, therefore, to be a material the components of which are in a state of equilibrium, and this accounts for its uniform composition. It is, therefore, a unique material, and it is to the large amount of surface energy developed by the highly divided mineral matter which it contains that the demonstrated industrial value of the asphalt is to be attributed.

The Introduction of Colloidal Clay into the Purer Forms of Bitumen.

In the light of the preceding facts the inference was drawn by the writer that clay in a colloidal state might be introduced in a similar manner, indus-

trially, into the purer forms of asphalt, and into the residual asphalts prepared from petroleum. For this purpose, a paste of clay and water, in which the clay was in a colloidal state as regards the water, was emulsified with residual asphalts from various types of petroleum. The water was then driven off at high temperatures and it was found that the relation of the clay to the bitumen became a colloidal one. The proportions were so selected that the resulting material, after the removal of the water, should consist of 67 per cent bitumen and 33 per cent of clay. These materials were then maintained in a melted condition in tubes for 24 hours, at a temperature of 325° F. The sedimentation which ensued, with the reduction of the viscosity of the continuous phase at this high temperature, varied with the different residuals, and was as follows:

TABLE 2.—*Sedimentation of Asphalt-Clay Mixtures.*

Source	Penetration	Colloidal Matter Per Cent Before Subsidation	Colloidal Matter Per Cent After Subsidation	Sedimentation Per Cent
Trinidad Residual	50	33.5	33.7	0.0
Bababui Residual	48	32.4	30.1	7.0
Mexican Residual	50	33.3	27.2	18.3
California Residual	50	31.8	23.8	25.2
Mid-Continental Semi-Paraffin Residual	51	33.8	21.7	35.8

It is apparent from the preceding data that the colloidal capacity, if it may be so designated, of the different materials is characteristic of the particular bitumen and its viscosity at a definite temperature. The various bitumens are, in this way, very plainly differentiated.

INDUSTRIAL APPLICATION.

Industrially these observations are of importance, especially in the construction of asphalt pavements, such as that laid on the Victoria Embankment in London. The mineral aggregate of this surface consists of fine sand, a filler for the voids in the sand, Portland cement, and the mineral matter afforded by that present in the Trinidad lake asphalt cement which forms the cementing or binding material of the surface. Experience has shown that the stability of such a surface under heavy traffic is dependent on the amount of surface energy developed by the mineral aggregate, that is to say, by the state of subdivision of the particles composing this aggregate. While this will depend upon the size of the sand particles and of those composing the filler, it is also contributed to by the highly developed surface of the colloidal components of Trinidad asphalt and to an extent which would be entirely lacking if the purer forms of bitumen were used with the aggregate, a fact which has been demonstrated by the difficulties which have been encountered in the construction of asphalt surfaces with the residual pitches, free from colloidal mineral matter, which have been met with in the past decade in England, and which have necessitated the employment of various expedients to overcome them.

The relation of surfaces of solids to films of liquids, especially when the surface is developed to such an extent as occurs in material in a colloidal state, has been demonstrated, therefore, to be a matter of supreme importance in carrying out successfully the construction of asphalt roadways to carry intense traffic.

A more detailed account of the colloid chemistry of asphalt is given in the following paper: C. Richardson, "The Colloidal State of Matter in Its Relation to the Asphalt Paving Industry," *Minn. Eng. Soc.*, May (1917).

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Colloid Chemistry of Petroleum

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Bancroft has adopted a flexible definition and classification of colloid chemistry, namely, that it is the chemistry of bubbles, drops, grains, filaments and films.

In approaching the subject of the colloid chemistry of petroleum, one must consider it in the light of a broad definition. There is no fine line of demarcation between molecular dispersions and the so-called colloidal dispersions on the one hand, and between colloidal dispersions and coarse suspensions on the other. Likewise, it is difficult in some cases to determine whether a process may be properly classified as colloidal. It is quite obvious to one with even a superficial knowledge of the subject that petroleum itself, especially the asphalt base types, is a colloidal system. One does not go very far in the refining of petroleum without recognizing that in many cases the processes as well as the products may be classified as colloidal. Oil field emulsions and asphalts are distinctly colloidal systems. The dispersion of wax in a crude oil or one of its fractions; fluorescence in lubricating oils and kerosene distillates; the removal of asphalt either by adsorption with solid adsorbents or by precipitation with sulfuric acid or other refining agents; the formation of color and gum in cracked hydrocarbon distillates; the dispersion of dyes in gasoline; the making and breaking of greases, are all colloidal phenomena. Emulsified lubricating oils, insecticidal sprays, asphalt emulsions, petroleum jellies or petrolatum (vaseline) are examples of some petroleum products having colloidal properties.

Paraffin base oils usually contain colloidally dispersed waxes, which assume crystalline form after distillation. It is probable that the action of heat during distillation changes the degree of dispersion or state of aggregation of the wax. Asphaltic base oils contain dispersed bituminous solids, probably derived from hydrocarbons by oxidation, sulfuration or condensation. Such colloidal asphalts may be reversibly precipitated, or by means of strong acid may be irreversibly coagulated.

It is highly probable that the coloring matter in petroleum and its distillates, including cracked distillates, is in a highly dispersed colloidal condition. Petroleum oils are generally optically heterogeneous, and in many cases show a Tyndall cone effect.

Ostwald [1] considers the high boiling petroleum fractions as iso-colloids. Pyhälä [2] looks upon crude oils as sols in which the dispersed phases such as asphalt are solid gels, the phenomenon of gelation occurring when the dispersed phase exceeds 60%. This latter statement is of course true of some types of oil only. Holde [3] considers the heavy opaque mineral oils as solutions of asphalts and resins in mineral oil. When dissolved in benzene such oils behave as colloids.

Dunstan and Thole [4] have shown that petroleum oils are optically heterogeneous. For example, the reddish yellow machine oils and white paraffin oils

display a bluish cone of light owing to the presence of colloidally dispersed particles. High concentrations of crystallized paraffin dissolved in benzene likewise show a cone of light, although the lower concentrations do not display this phenomenon.

Dunstan [5] * states that the formation of acid tars in the treatment of hydrocarbon oils with sulfuric acid is probably a dual phenomenon—firstly, the acid coagulates the colloidal matter in the oil, and secondly it brings about polymerization of olefins and diolefins; and sulfonation of aromatic derivatives together with oxidation of primary materials and products. Dunstan [6] also points out that there is a peculiar hysteresis effect in the viscosity of fuel oils and that by a suitable alteration in the previous history of a given oil wide variations in its viscosity may be effected similar to the behavior of aqueous gelatin sols.

Schulze [7] postulated that the color in petroleum is due to an oleosol, of high molecular weight, containing oxygen, sulfur and nitrogen. The mechanism of refining is a precipitation of resinous pitchy and asphalt material, held as colloids, with sulfuric acid. Condrea [8] on the other hand claims that refining is due to polymerization and oxidation by sulfuric acid of colored decomposition products formed during distillation. The compounds formed by such treatment are dissolved in the acid. He does not agree with the theory of precipitation of colloidal material. Schulze [9] in reply to Condrea states that zinc chloride is a good polymerizing agent for unsaturated hydrocarbons and still does not have the same refining action that filtration through fuller's earth has.

Crude Oil Emulsions

One of the great problems of the petroleum industry is the handling of emulsified or "cut" oil. In practically every oil field, especially those producing asphaltic crudes, a considerable proportion of the crude comes to the surface in emulsion form. This emulsion may be thin and mobile, or it may be a pasty solid, practically impossible to transport by pipe line and troublesome if not impracticable to refine. Large amounts of emulsified oil have been burned as a waste product, due to the difficulty of transporting and refining it. Crude oil emulsions are still burned in some localities. Some is run into sumps. It is reported that some crude oil emulsions have been in such storage for over twenty years. It is estimated that in 1930 three hundred million barrels of the world's total crude oil production was produced in emulsion form, and required some form of treatment before it could be marketed.

Properties of Petroleum Emulsions

In appearance petroleum emulsions vary greatly. Some are quite fluid and readily handled. Others are viscous, and some are pasty or gelatinous and can be handled only by shovel. Wright [10] describes a case, "wherein an oil of 25° Bé. has taken up and held over 75 per cent of water and foreign matter in so thoroughly an emulsified form that it has stood for a number of years without the water settling out. This emulsion, as produced, is extremely viscous, reddish brown in color, and of a jelly-like consistency, having a gravity between 10° and 11° Bé. and as observed when flowing from the well, from which it is emptied not in a stream but in chunks, it resembles raw liver. It is needless to say that this emulsion is absolutely worthless, and that the greatest problem it entails is its disposition, as its transportation by pipeline is practically impossible because of the high viscosity of the mass."

* *See paper by Dunstan in this volume. J. A.*

Naturally occurring petroleum emulsions are usually of the water-in-oil type or of mixed types. Cases are on record, however, of emulsions of the reverse type, in which the oil was the internal phase. By addition of suitable chemicals the phases in petroleum emulsions can be reversed in some cases. Waste water from oil wells is in most cases an emulsion of minute droplets of oil suspended in water.

The suspended globules of water in the usual emulsions vary greatly in size, ranging from true colloidal dimensions, about 0.00001 mm. (10 $m\mu$) in diameter, to droplets of several millimeters diameter. It is probable that the largest particles are not truly emulsified but are mechanically suspended in the emulsion. As would be expected, emulsions containing large water droplets are less stable than those in which the water is more finely divided. The water particles, as observed under the microscope, appear to move freely in the oil, and one can usually observe that they show the Brownian movement. When droplets are brought into contact there is a definite resistance to coalescence, and they appear to be surrounded by enclosing films which are ruptured only with great difficulty. If mechanically distorted, the droplets tend rather to break up into smaller particles than to coalesce.

The substances found in petroleum which appear to act as emulsifying agents include asphalts, resins, naphthenic acids, hydrocarbons of high molecular weight, and finely divided solid substances such as clay. The organic substances mentioned, being soluble in the oil, forming either true or colloidal solutions, would be expected to produce water-in-oil dispersions, which is the type of most petroleum emulsions. The emulsifying agent often separates at the oil-water interface as an elastic film visible under the microscope. An indication that asphaltic material in oil is in colloidal rather than true solution is the fact that at times it may be separated by filtration, leaving an oil which does not emulsify.

That asphalt has emulsifying properties is also shown by its tendency to remain largely in the emulsion layer. Moreover, asphalt separated from emulsified crudes is able to emulsify kerosene and water.

The ash from crude oil emulsions has also been found to be an emulsifying agent for kerosene and water. This makes it probable that the finely divided inorganic substances suspended in petroleum are responsible, in part at least, for its emulsifying properties. Dissolved salts in the water phase may influence emulsification by causing slight flocculation of asphalt or resin at the oil-water interface to form stabilizing films around water droplets.

Breaking Emulsions

A tremendous amount of study has been devoted to the breaking of crude oil emulsions. The major methods which have been tested in commercial practice are: (1) Settling; (2) heating or distilling at atmospheric pressure; (3) heating or distilling at elevated pressure; (4) action of electricity (electrical dehydration); (5) use of chemicals; (6) centrifuging; (7) filtration.

The method used to de-emulsify for any given oil emulsion depends upon the type of oil and the tenacity of the emulsion.

Settling. When oil containing both emulsions and free water is allowed to stand in a tank or sump, break-down of the emulsion sometimes occurs. Usually, however, there is a separation into an oily layer, a layer containing emulsified oil, and a layer of water. The free oil is pumped from the top and passed to storage.

Heating at atmospheric pressure. In some cases emulsions may be

broken by gentle heating, in storage or special open tanks, by means of a steam coil. This is a wasteful and unsatisfactory method. Emulsified oil may be distilled at atmospheric pressure in either shell or tube stills. This is a slow, tedious and expensive process with the ever-present risk of the still foaming over, or in the parlance of the oil refiner the still "pukes."

Heating or distilling at elevated pressure. Pressure distillation in either shell or tube stills is the most generally applicable of all methods for the breaking of crude oil emulsions. It is rapid in action and eliminates the danger of foaming or puking. Very stable California emulsified crude oils have been successfully distilled under moderate pressure at a rate as high as ten times as great as that possible under atmospheric pressure in the same apparatus. The pressure distillation and condensation of the vapors of emulsified oils at elevated temperatures can be carried out not alone to dehydrate oil but also to crack it into motor fuel.

Electric dehydration. The use of electricity in the dehydration of emulsified oil has developed from the work of Cottrell on the electric precipitation of solid particles suspended in air or other gases, such as fog or smoke.* An alternating current with a high potential difference is employed. In the application of the alternating current the field is continually reversing so that the only tendency is for the irregularly distributed globules of water to arrange themselves along the shortest lines between the electrodes. The globules form chains and gradually coalesce along these chains. The direct current method is also used in dehydrating oils.

Chemical treatment. There are several groups of chemical reagents employed in the dehydration of crude oil emulsions. Among these the most satisfactory is the addition of substances which tend to break the protective emulsion films by their tendency to form emulsions of the opposite type from that present in the oil. Among the chemical substances which have been proposed for the breaking of emulsions, the following may be cited:

(1) Dehydrating agents such as calcium chloride and quick lime.

(2) Agents which presumably cause flocculation of the substances composing the protective films and thereby cause coalescence of the water droplets, such as sodium chloride, ferrous sulfate, sodium sulfate, etc. These have not proved very effective.

(3) Substances which presumably react with salts or organic acids present in the external phase of the film, such as caustic soda, lime, sodium bicarbonate; for example these may react with naphthenic and other acids to form water-soluble soaps and the water-in-oil emulsions will tend to be reversed and thus broken.

(4) Substances which tend to break the protective films by their tendency to form an emulsion of the opposite type from that present in the oil. This group includes iron oxides and other finely divided salts, such as clays, silica, soaps, gums, starches, albuminous matter, etc. In general these substances tend to stabilize oil-in-water emulsions and thus to break water-in-oil emulsions. The finely divided solids, when effective, probably act in the same manner, since it is well known that some finely divided solids are good emulsifying agents for oil-in-water emulsions.

(5) Electrolytes, which presumably neutralize the electrical charge of the emulsified water droplets. Among these are acids such as sulfuric acid, acetic acid and salt solutions, such as ferric nitrate and ferric chloride.

(6) Solvents which dissolve the material making up the protective film of the emulsion. Among such substances are carbon disulfide, carbon tetra-

* *See* paper on this subject in this volume by W. W. Strong. J. A.

chloride, benzol, acetone, alcohol, ether and gasoline. Besides their solvent action they tend to decrease the viscosity of the external phase and thus reduce the stability of the emulsion. In general, these solvents are used to break emulsions only on a laboratory scale for determination of the water content of the emulsion.

Commercial de-emulsifiers in general act like one or several of the groups mentioned. Chemical treatment of crude oil emulsions has been quite effective on a large scale either alone or used in combination with some of the other methods of breaking emulsions herein mentioned.

Centrifuging. Centrifuging is used in the dehydration of crude oil emulsions but chiefly in combination with some other method of dehydration; for example, heat or chemical reagents.

Filtration. In some cases crude oil emulsions may be resolved into their components by passage through a filter. When the filter is more readily wetted by the water than by the oil, separation is facilitated.

While many methods have been used with success for the breaking of crude oil emulsions, there is still room for improvement in breaking crude oil emulsions, as well as for the breaking of bottom settlings and other emulsified materials which accumulate in the refinery.

Refining by Adsorption

Many materials are used in the refining of oils by various adsorbing agents. In general the materials are of a porous structure, the pores being of the continuous type. Various earths and minerals such as fuller's earth, china clay, kaolinite, alumina, bauxite, magnesite, iron oxide and various alkaline earth oxides such as calcium and magnesium oxides. Other materials such as bone ash, bog iron ore, Death Valley clay, bentonite, silica gel and various carbonaceous materials such as coke, coal charcoals of various types such as bone-black, wood charcoal, blood charcoal, etc., have all been used or mentioned in the literature as being used in connection with the refining of oils.

Gurwitsch [11] * has pointed out that adsorption can be accompanied by purely chemical processes such as the polymerization of unsaturated substances. For example, amylene can be changed by the action of hydro-silicates similar to fuller's earth or charcoal to dipentene and other compounds. Hexylene acts in a similar manner.

Venable [12] showed a similar phenomenon with pinene or turpentine, which when treated with fuller's earth from dipentene and terpinene.

Phalen [13] states that the bleaching action of fuller's earth is independent of its chemical composition and depends on the power of selective adsorption.

Rohland [14] states that the best clays are the dark plastic type containing the hydroxides of silicon, aluminum, iron and titanium as colloids. He found certain clays are impermeable to chloroform, carbon bisulfide, petroleum ether and saturated hydrocarbons, but adsorb unsaturated hydrocarbons of both the ethylene and acetylene series. Oxygen-containing substances such as water and alcohol are taken up, whereas the oxygen-free substances such as benzene and toluene are hindered.

Wesson [15] states that the efficiency of fuller's earth can be determined only by actual test and that a chemical analysis is of little value. The presence of soluble iron salts should be detected, these salts having an oxidizing action. This statement is made with reference to vegetable oils. He also states that bleaching is a function of the degree of hydration of complex silicates.

* *See* paper by Gurwitsch in this volume. J. A.

Guiselin and Handicourt [16] state that petroleum and its products on filtration through argillaceous earth undergo fractionation first. The same authors [17] make the statement that the earth acts both by adsorption and by mechanical absorption and that unsaturated compounds seem to be strongly adsorbed.

Gilpin and Schneeberger [18] look upon petroleum as a two-phase system, that is, an emulsion in which the fuller's earth acts as a dialyzing septum permitting free passage of paraffin oils and causing adsorption and coagulation of the bitumens, carrying with it sulfur and nitrogen compounds and the unsaturated hydrocarbons.

Baines, *et al.*,[19] treat mineral oils with adsorbent substances such as wood charcoal, powdered coke, lime, earth, clay, pumice, etc. In the practical operation of the process, according to the specifications, it has been found desirable to send the vapors through the dry adsorbing material previously soaked in a solution of zinc chloride.

Dunstan [20] examined the decolorizing properties of various adsorbent and decolorizing agents using a 0.25 per cent solution of crude asphaltic oil in benzene, obtaining the following results:

Material (1 Gram)	Cubic Centimeters of Colored Solution Decolorized
Alumina	60
Fuller's earth I	30
Bauxite I	30
Bauxite II	25
Bauxite III	20
Ignited peat	15
Bone charcoal	14
Bog iron ore	12
Fuller's earth II	10
Ferric oxide	10
Ball clay	8
Fuller's earth III	8.5
Fuller's earth IV	4
China clay	2
Kieselguhr	2

He states that cold bauxite which has been ignited and cooled in a vacuum desiccator was found to have lost its power of adsorption in the treatment of kerosene, but when freshly heated to 200° C. it was reactivated. Heat appears to be evolved during active adsorption; thus a 20° C. rise in temperature was observed during the passage of 100 cc. of kerosene through 50 grams of bauxite. The degree of fineness of the adsorbent is an important factor in treating.

Dunstan [21] showed that Floridin, fuller's earth and bauxite, when freshly ignited, possess adsorptive properties following the well-known adsorption rule, $Y/M = ac^{1/n}$.

One of the most successful processes used in treating gasoline generally, including some classes of cracked distillates, is the Gray vapor phase treating process, which consists in passing the vapors to be treated through fuller's earth. The equipment used in this system is either a single fuller's earth of so-called "clay" tower followed by a knock-out box or bubble tower, or combinations of these.

The vapors from the still enter the top of the tower and pass through the "clay." The vapors leaving the bottom of the tower may then pass through a "knock-out" box, the main purpose of which is to remove any of the entrained liquids or polymers. The vapors leaving the "knock-out" box pass

through a condenser coil and then to a storage tank. The best results have been obtained by passing the vapors through a small bubble tower after leaving the clay tower. In passing through the clay, the undesirable compounds are polymerized by the action of the fuller's earth.

In some cases a small amount of steam is used continuously in the top of the tower, while in other operations the clay is steamed heavily periodically as found necessary, or the two operations may be combined. It is general practice to spray a small amount of gasoline into the top of the tower. This is useful in that it assists in washing the clay free of polymers.

With this vapor phase treating process there is very little, if any, reduction in the sulfur content of the gasoline. The gum content in the finished gasoline has a tendency to increase as the gasoline treated per ton of clay increases.

Adsorptive materials may be used both in the liquid and vapor phase, either alone or in conjunction with other substances. There are many patents issued on the application of adsorbents to refining.

Aside from the purely adsorptive methods of treatment, polymerizing agents may be used, such as the salts of heavy metals, either as such or in solution, for treating the oil in the liquid or vapor phase.

Recovery of Gasoline by Adsorption of Vapors from Gases

One of the best examples in the petroleum industry of the practical and commercial application of the adsorption of a vapor from a gas by a solid is the charcoal process of extracting gasoline from natural gas or refinery gases. This process was a development of the World War and makes use of activated charcoal such as was used in gas masks. The process was patented by Burrell, Oberfell and Voress.[22] Briefly, the process consists in passing gases containing gasoline through a column containing activated charcoal. The adsorbed gasoline is distilled from the charcoal by means of steam and then condensed. Three adsorption units are used successively in the process, in one of which adsorption and in a second distillation are effected, while the third is kept in readiness for the adsorption process. When the charcoal shows signs of lowered activity it is reactivated by treatment with superheated steam. It is to be mentioned here that the oil absorption process for gasoline recovery, particularly when operated under superatmospheric pressure, is used much more extensively than the charcoal recovery process.

Refining Petroleum by Chemical Methods

The foregoing discussion has developed some of the colloidal aspects of refining, particularly in regard to the use of adsorbing agents. The chemical treatment of hydrocarbons introduces various problems of a colloidal nature, particularly in regard to emulsion formation. For example, in the treatment of low boiling oils such as cracked distillates, gasolines, naphthas, and the like, with sulfuric acid and water followed by neutralization with alkalis such as solutions of sodium hydroxide alone or containing litharge dissolved therein, emulsion formation presents a serious economic problem. Similar problems are presented in the treatment of lubricating oils.

Treatment of hydrocarbon oils generally with sulfuric acid results in sludge formation, the character of the sludge depending upon the oil undergoing treatment, the conditions of treatment and concentration of the acid. With lubricating oils the sludge may be viscous, semi-solid or even solid, whereas with light distillates, particularly those containing only a small per-

centage of unsaturated hydrocarbons, the sludge is of a distinctly liquid character. With cracked distillates the sludge varies from a fluid to a viscous liquid depending upon the variables mentioned.

After agitation of the oil with sulfuric acid some of the sludge separates out immediately upon standing while a portion will remain suspended, usually in a finely dispersed condition, but in some cases the dispersion appears to be of a molecular type. Immediately after the agitation, particles of sludge may be seen coalescing and forming relatively larger globules from the highly dispersed particles. The rate of settling of some of the particles is very slow. The presence of any appreciable amounts of sludge during water washing and neutralization with an alkaline solution, causes the formation of undesirable products of hydrolysis which is practically equivalent to the reversal of the beneficial effects of refining. Such difficulties are encountered particularly with cracked distillates and lubricating oils, making it necessary in some cases carefully to select the proper concentration of acid and to predetermine the temperature of treatment as well as to allow a sufficiently long time to permit complete settling of the sludge.

In some cases special methods are resorted to for the removal of suspended sludge, such as the addition of adsorbent materials, particularly fuller's earth. This is quite common practice in the treatment of lubricating oils, cracked distillates, kerosene and other products. Such treatment is trebly beneficial, as neutralization is effected, the final traces of the so-called pepper sludge are removed, preventing the ill effect of hydrolysis by washing with water and alkalis, and emulsion formation is prevented.

More recently processes have been devised for the immediate removal of sludge from an acid treated oil by centrifuging. This has the advantage of preventing further undesirable reaction between the sludge and the oil.

During the water-washing step emulsions are formed, particularly if the mixture is vigorously agitated. For this reason water wash by spraying is preferred to an orifice or a mechanical mixer for this step. Treatment of acid-treated oils with alkalis makes the oil particularly susceptible to emulsion formation. In the case of lubricating oils such emulsions are readily formed, and special steps must be taken to avoid emulsion formation, or for the breaking of these emulsions by, e.g., the addition of soap solutions. Emulsion formation also occurs in the steam distillation of petroleum, especially with the neutral lubricating distillates and overhead cylinder stocks.

Chemical Treatment of Petroleum Distillates

The continuous treatment of cracked distillates comprises mixing the distillate with sulfuric acid, settling the acid in a chamber, separating the sludge, causing the distillate to overflow to the water-washing chamber where it is contacted with water by spraying, separating the water by settling and causing the substantially water-free distillate to overflow into a mixing column, where it is contacted with a solution of alkali, and subsequently separating the alkali.

An extensive study was made of emulsion formation in the treatment of cracked petroleum distillates. The study was divided into several phases, namely, emulsion formation following: treatment with sulfuric acid; water washing subsequent to the removal of acid sludge; and emulsion formation following treatment with caustic solutions for neutralization.

In practically all cases noted, even with settling periods up to one hour, a substantial amount of pepper sludge remained in the oil following the acid treatment. The oil leaving the water-wash chamber following the acid treat-

ment was milky in appearance. The oil leaving the caustic settling chamber is invariably alkaline and usually shows a fine dispersion of caustic solution. The following figures show the amount of water remaining in the oil at varying rates of water wash, maintaining fairly constantly the rate of oil fed to the plant. The oil was settled for one hour in all cases.

Gallons oil feed per minute	175	180	175
Gallons water feed per minute	86.5	60	69
Oil in wash water after settling acid sludge	0.28%	0.16%	0.16%
Rate of feed water wash following caustic settling gallons per minute	17.7	19.5	32
Oil in wash water following caustic	0.21%	0.08%	0.04%
Water from sump (waste water tank)—gallons per minute	104	...	101
Oil in water from sump	0.08%	0.06%	0.02%

In another set of representative tests cracked distillate fed at the rate of 90 gallons per minute showed the following results at different rates of water washing after settling the acid sludge. The time of settling here was one hour also.

Gallons per minute of water used for washing	6.3	9.9	11.0
Per cent oil which separated from the water after 24 hours	0.14	0.13	0.14
Per cent acidity of pressure distillate before washing	0.106	....	0.135
Per cent acidity of pressure distillate after washing	0.042	0.048	0.089
Per cent acidity of washed water	1.22	1.38	1.27

The above are generally representative of results obtained with fairly well-designed and operated treating plants. The pressure distillate leaving the acid settling tank usually contains a substantial amount of finely dispersed "pepper" acid, most of which settles on standing from one-half to one hour. The pressure distillate leaving the water-wash tank after acid treatment, was hazy in appearance. Upon standing in a test bottle drops of moisture settled. This moisture had a distinct acid reaction. The pressure distillate leaving the caustic settling tank gives a distinctly alkaline reaction and on long standing drops of caustic settle out. The pressure distillate leaving the final water-wash tank was apparently neutral.

The water leaving the water-wash tank following the acid treatment has a pearly appearance and was acid in reaction. After standing for three hours oil began to accumulate on the top of the water, and continued to collect for about 24 hours. The water did not clear up but remained milky even after standing for three or four days. This water carried from 0.16 per cent to 0.28 per cent of oil, which separated out. A sample of the water which had stood for four days was centrifuged for two hours but did not show any signs of clearing. Upon the addition of caustic a fluffy precipitate formed and the water became clear. There was no oil on top of the water, however, upon clearing.

The wash water following the alkaline treatment had a slightly milky appearance which was completely cleared up upon standing. This water carried from 0.04 per cent to 0.02 per cent oil which accumlated on top of the water.

The water leaving the sump was milky in appearance and was found to contain from 0.02 per cent to 0.08 per cent of oil which accumulated on top of the water. The water did not show any signs of clearing upon standing, nor after centrifuging for two hours. It was alkaline in reaction and did not clear up upon the addition of acid and centrifuging.

The spent caustic from the caustic settling tank was dark brown in color. Upon standing three days a heavy, oily, reddish substance collected on the bottle at the top of the caustic.

Removal of Suspended Lead Mercaptides and Lead Sulfide from "Doctor"-Treated Cracked Distillates

Some interesting colloidal phenomena are involved in the sweetening of light distillates by the so-called doctor treatment, consisting in treating the distillate with a solution of litharge in caustic soda solution (sodium plumbite) forming lead mercaptides, which are subsequently converted to the corresponding disulfides and lead sulfide by the addition of elementary sulfur.

The lead mercaptides remain in various stages of dispersion, including molecular, colloidal, and coarse suspensions. Analyses of the precipitates after adding sulfur show the presence of a considerable percentage of lead mercaptides. Experiments show that sulfur precipitates a substantial proportion of the higher molecular weight mercaptides *per se* in addition to converting them to the corresponding disulfides. The lower molecular weight mercaptides are almost completely converted to the corresponding disulfides. The lead sulfide formed by this reaction may also remain in a finely dispersed condition. Apparently there occurs some adsorption of the elementary sulfur added. Finely divided adsorbent earths may also be used to remove suspended mercaptides and lead sulfide.

Refining Lubricating Oils

Adsorption methods are used in the refining of lubricating oils consisting in filtering the products directly through a bed of adsorptive earth, such as fuller's earth, or of suspending and subsequently agitating some of the adsorptive earth in a finely divided condition in the oil. This treatment may be applied directly, but more usually follows the acid treatment.

The contact process for the refining of lubricating oils consists in treating the oil with sulfuric acid and subsequently neutralizing and further refining the oil by contacting it directly with finely divided adsorptive earths such as fuller's earth or activated clays. The clays neutralize the excess acid and sludge which is not removed by settling. The finely divided particles of acid sludge as well as coloring matter in the oil itself, are removed by adsorption. In the neutralization of lubricating oils with solutions of alkalis following acid treatment, considerable trouble is encountered in the formation of very stable emulsions, and one of the common methods of breaking these emulsions is by salting or by the addition of a soda soap. The soap dissolves in the alkaline solution, thereby lowering its surface tension and promoting its tendency to emulsify the oil which causes the breaking of the water-in-oil emulsion.

Sodium salts of naphthenic and sulfonated naphthenic acids present in the treated oil markedly effect the emulsification of lubricating oils.

Cylinder and bright stocks are usually neutralized by direct contact with clays, following acid treatment. Owing to their tendency to emulsify, used lubricating oils are recovered usually by diluting with naphtha, contacting with adsorbent clays, filtering and subsequently distilling off the naphtha.

Lubrication

For some lubrication purposes, particularly for use in steam engines with oil circulating systems, lubricating oil must not readily form emulsion, as emulsification would greatly reduce its usefulness. The resistance to emulsifi-

cation is in part an original property of the oil and in part a result of proper refining. For other uses, as in engines in marine service, oils are emulsified and have suitable lubricating value in emulsion form. According to Dunstan [23] the addition of free fatty acids in the process of Southcombe and Wells, according to whether the fatty acids are low or high in molecular weight, will render the oil non-emulsifying or emulsifying.

Treatment of Cracked Residual Oils for the Production of Lubricating Oils

J. C. Morrell [24] makes use of sulfuric acid or a sludge resulting from the treatment of hydrocarbon oils with sulfuric acid to remove the suspended pitchy or coke-like material in cracked residual oils. Depending upon the concentration and amounts of sulfuric acid as well as temperature, precipitation of the asphaltic components as well as the suspended particles may occur.

The supernatant liquid from the complete precipitation of suspended carbonaceous material and asphaltic matter is suitable for the production of lubricating oils. The untreated material is a deep brown, while the supernatant oil is greenish brown.

As an example of the application of the process to the manufacture of lubricating oils, a cracked residual oil was treated at a temperature of approximately 200° F. with approximately 5 per cent by volume of a sludge acid resulting from the treatment of a cracked distillate with sulfuric acid. Approximately 80 per cent by volume of supernatant oil was recovered, the precipitate being a dense coke-like mass. The clear liquid was neutralized by filtration through a column of lime, and was then redistilled in the presence of steam or under reduced pressure. The lubricating oils produced by this treatment had the following characteristics:

	Light	Medium	Heavy
A. P. I. Gravity	17	16.2	14.2
Flash Point	290° F.	305° F.	430° F.
Fire Point	370° F.	385° F.	500° F.
S. U. Viscosity at 100° F.	105 sec.	300 sec.	820 sec.

In addition to the production of lubricating oil distillates, a kerosene distillate and gas oil cut is produced. A small amount of asphaltic material remains from the distillation of the supernatant liquid having in general the properties of gilsonite. Varying amounts of lubricating oils were recovered depending upon the type of residuum treated, varying from 30 per cent to 40 per cent of the oil treated. The remaining oil comprised refined burning distillates such as kerosene, furnace and gas oil. Vacuum distillation of the treated oil gave best results in regard to lubricating oil products; and the products could be further improved by filtration through fuller's earth.

Separation of Wax from Petroleum Products

One of the important operations in the manufacture of lubricating oils is the separation of the wax contained therein, or in the intermediate products from which the lubricating oils are derived. The presence of wax in lubricating oils causes them to congeal at low temperatures and may render them unfit to use during cold weather. The removal of wax from petroleum products is thus an important operation.

Refinery operators generally recognize two forms of wax, namely, amorphous and crystalline. Generally the wax precipitated from residual oils is

of the amorphous variety, while those from distillate lubricating stocks may be either amorphous or crystalline. The removal of crystalline wax is a relatively simple operation, namely, by filter pressing; the slack wax so produced offers very little difficulty in the sweating operation.

Usually waxes are prevented from crystallizing because of the presence of colloidal bodies of a resinous or gummy character which prevent the growth of the crystal by forming a film over the highly dispersed small crystals.

Engler and Bohm's [25] conclusions are that paraffin in mineral oils consists of two forms, namely, amorphous which is transformed into the crystalline state by distillation, and completely formed crystalline paraffin. Zaloziecky [26] arrives at the same conclusion and refers to the amorphous paraffin as protoparaffin. The latter is said to consist mainly of isomers of the normal paraffins. The other form he refers to is pyro-paraffin, which consists mainly of the normal hydrocarbons. He claims to have shown that there is actually a formation of paraffin during distillation of the residue.

Partridge [27] after various experiments arrived at the conclusion that the two types of paraffin are identical. He gives as his opinion that the amorphous paraffin is inhibited from crystallizing owing to the presence of colloidal oil matter. This point of view appears reasonable to the writers. Pawlewsky [28] along the same lines assumes paraffin in crude oil to be in a colloidal state similar to petroleum jelly. He cites the separation in colloidal form from such solvents as xylene and chloroform, while on the other hand the paraffin assumes the crystalline form when separated from acetic acid and other solvents.

It appears from the above that in reality the so-called differences in type of paraffin may be due simply to a difference in state of aggregation, and that the amorphous variety may be paraffin in a highly dispersed state which is prevented from crystallizing owing to the presence of other substances.

Padgett, Hefley and Henriksen [29] made extensive studies in regard to the crystallization of waxes from lubricating oil stocks and noted three types of crystallization, all of which have a bearing on the practical operations of refining. The following is quoted from these authors:

> "One type is that characteristic of residual oils, petrolatum, and heavy raw-wax distillates. The crystals from these products are small and are made to grow with difficulty, even after substantial removal of associated bitumen. The wax separated from petrolatum by precipitating five times with acetone showed an improvement in crystallization over the original petrolatum and the wax after the second precipitation; but the crystals were still much smaller than those from slack wax cooled under the same conditions, and the mode of crystallization was different. Under different conditions, to be described in a later paper, the wax secured from petrolatum by precipitating five times with acetone formed much larger crystals, comparable in size with those from slack wax. The crystals, however, were plates instead of needles."

Padgett and his co-workers concluded "that the actual nature of the waxes is of considerable importance in wax crystallization, although the associated substances such as the oily and asphaltic material and the presence of different waxes in admixture with one another must not be overlooked."

The factors bearing upon crystallization of waxes from lubricating oils apply also to the physical distribution of waxes in residual oils such as fuel oils, whether of a straight run or cracked character. In residual oils of this type, particularly those from asphaltic stocks or those which contain a high percentage of asphaltic matter resulting from cracking, crystallization of the wax is inhibited to a large extent by the asphaltic matter present.

A peculiar phenomenon observed in connection with the congealing of

oils has been noted, namely, when such oils are heated to relatively high temperatures and then rapidly cooled, the congealing temperature is many degrees below that observed on the normally tested or treated oil.

Sweating of Wax

The crude slack wax produced by filter-pressing waxy distillates consists essentially of a coarse dispersion of the oil in the wax. The slack wax is placed in a series of pans in a so-called sweat house and is melted by means of steam-heated coils. Cold water is circulated through a separate set of coils, which congeals the wax and permits the removal of the oil. A further separation of oil from wax crystals may be effected by regulated circulation of heated water. The main portion of the solid wax is collected on screens and the separated oil removed. The wax is subsequently melted and filtered through a column of fuller's earth to remove suspended and dissolved colored impurities. Padgett, Hefley and Henricksen [80] studied the sweating of wax. In the purification of the slack wax they noted at first centers of crystallization of various shapes (triangular, rounded, pentagonal, etc.), from which fine needles sprout in various directions. These needles, under temperature control, grew in length and breadth, producing the interlacing condition peculiar to slack wax. This mode of crystallization is peculiar to the products high in wax concentration, such as slack wax and the crude and refined waxes. The crystallization of cracked wax distillate is different in that the needle formation from centers is not so marked. The sweating of wax is an example of fractional fusion.

Lubricating Greases from Petroleum

Lubricating greases are water-in-oil emulsions stabilized by a soap. As specific examples of preparation, the oil is mixed with a fatty acid or fat and this is added to the soda solution, using approximately 5 per cent of soda solution to 15 parts of fatty acid and 80 parts of oil. Cup grease is made by mixing a soap which may be a lime, magnesium, sodium or aluminum base, made from animal or vegetable fat, with mineral oil and a small amount of water. The water aids in bringing about the proper consistency and preventing separation of the soap. The proportion of water used roughly parallels the soap content. The physical properties and usefulness of such a grease are determined by its colloidal characteristics which are determined by the ingredients, and method of preparation. The rate of cooling and other conditions during solidification after manufacture are particularly important.

In the manufacture of greases three principal components are required, namely, a saponifiable oil or fat, a mineral oil, and an alkali, which in most cases is lime. The oil or fat may consist of the fat itself or a fatty acid derived therefrom. The kind of fat used varies widely, each having its own peculiar advantages and characteristics.

Cup greases are the most important of the grease lubricants, comprising over half the total production. In general, the saponifiable oils or fats may consist of animal or vegetable oils, including horse fat, hog fat and tallow, lard and tallow oils, fish oil, and whale oil. Various vegetable oils may be used, including those from palm, cottonseed, soya bean, castor bean, and rapeseed. Some bone fat, garbage greases and the like are also used. The fatty acids, such as oleic or stearic, may be used directly or in combination with various fats. The mineral oil base may consist of refined distillates or

special petroleum cuts or of petroleum residues. The mineral oil content varies from approximately 70 to 99 per cent of the grease.

From a colloidal viewpoint the greases are dispersions of water in a mineral oil containing a soap. The soap, being more soluble in the oil than in the water, produces the water in oil type of emulsion.

The question as to whether the grease itself is a lubricant or whether it lubricates only by virtue of the contained lubricating oil is one of controversy. It is known, however, that when greases are subjected to violent disruptive forces such as are found between a journal and its bearing, or even when stirred violently, they lose their gel nature and break down into oil and soap. The presence of water is apparently necessary to prevent syneresis, that is, the sweating of oil from the oil-soap gel, and the water in general stabilizes the system.

Calcium soap greases have a smooth appearance and lack elasticity. Calcium rosin greases (axle greases), when stirred or mechanically worked, break down more readily than the calcium soap or fat greases, and are more sticky than the corresponding fat greases. Anhydrous sodium soap greases are more fibrous in nature than the calcium soap greases and are more elastic. As would be expected, the sodium soap greases emulsify directly in water, with water as the external phase. The presence of water in a sodium soap grease destroys its fibrous nature and reduces the grease to a more or less low-melting paste. Soda-lime greases, that is, mixtures of the two kinds of soap are of an indistinct fibrous character. Aluminum soap greases are insoluble in water, smooth, sometimes translucent, and vary in physical characteristics, depending upon whether the stearates or oleates are used. Lead soap greases are smooth, adhesive and non-elastic.

Grease-making is at a stage where it is just emerging from the trade secret status and is a fertile field for investigation by the colloid chemist.

Asphalt

Naturally occurring asphalts as well as those made by the reduction of asphaltic crude oils represent colloidal systems.

Natural asphalt found in a deposit of many millions of tons in the crater of an old mud spring or geyser in the Island of Trinidad, British West Indies, is one of the unique phenomena of the world. The deposit consists of a complex system of several phases—gaseous, liquid and solid, composed of both organic and inorganic materials. The naturally occurring asphalt is in a highly emulsified condition with water as the internal phase, the protective agent being clay and other inorganic matter. The approximate composition of crude Trinidad asphalt as given by Richardson is as follows:

	Per Cent
Water and gas	29.0
Bitumen soluble in cold carbon disulfide	39.0
Bitumen adsorbed and retained by the disperse mineral matter	0.3
Mineral matter on ignition with tricalcium phosphate	27.2
Water of hydration of clay	4.2

Richardson [81] showed that a crude Bermudez asphaltic crude oil practically free from mineral matter could be readily emulsified with a paste of colloidal clay and water forming a system similar to that of the natural product.

Artificial asphaltic crude oil made by the reduction of crude oil either by steam refining or by subsequent air-blowing, has largely replaced the use of the naturally occurring asphalt. Crude oils are reduced to flux oils, which are

transferred to the asphalt still provided with steam and air lines. It is steam-distilled or air-blown until the penetration, ductility and melting points are satisfactory.

In the production of mineral rubber various percentages of gilsonite are added and the flux oil-gilsonite mixture is air-blown to the desired melting point.

Richardson [82] showed that the durability of an asphalt pavement is directly connected with the fineness of the mineral aggregate, that is, with the extent of the surface developed. Richardson [83] also showed that the stability of an asphaltic surface under heavy travel is dependent upon the amount of surface energy developed by the mineral aggregate, that is to say, by the state of subdivision of the particles composing this aggregate. While this will depend upon the size of the sand particles and of those composing the filler, according to Richardson it is also contributed to by the highly developed surface of the colloid components of Trinidad asphalt. Richardson states: "The relation of surfaces of solids to films of liquids, especially when the surface is developed to such an extent as occurs in material in a colloidal state, has been demonstrated, therefore, to be a matter of supreme importance in carrying out successfully the construction of asphalt roadways to carry intense traffic."

Asphalt and Bituminous Emulsions

One of the rapidly growing branches of the asphalt industry, which is in effect a branch of the petroleum industry, is that concerned with the production of asphalt emulsions. The emulsions contain as a rule 45 to 75 per cent of asphalt, 25 to 55 per cent of water and 1 to 10 per cent of an emulsifying agent. The origin of the asphalt—whether it be naturally occurring or from petroleum refining—is of no great importance, as nearly any asphalt may be satisfactorily emulsified. Each process, however, is adapted to emulsifying asphalts of varying characteristics.

Asphalt emulsions were first used for laying highway dust. They have gained in popularity until now they are used extensively in the United States and Europe for resurfacing, cold patching and maintenance work, and sometimes in new highway construction. An emulsion of this sort if not exposed to the atmosphere must remain liquid for a considerable period and must resist freezing. When applied it must flow freely, penetrate thoroughly and break down to leave a layer of asphalt. Asphalt emulsions are also used for waterproofing, binders or cements, in many applications for insulation, briquetting, paints, preparation of special paper, cardboard, fiber board, felt and similar uses. The introduction of the "colloid mill" has made it generally possible to produce some kinds of asphalt emulsions by direct dispersion of asphalt in water containing an emulsifying agent, usually a soap solution. Naphthenic acids, rosin, sulfonated oils, casein solutions, clays, alone or in combination, have been used.

As an example of one phase of the asphalt dispersion industry which shows the application of colloidal chemistry thereto, reference is made to the description of the Kirschbraun process by J. Miscall.[84] In the Kirschbraun process the molten asphalt is dispersed in a suspension of clay in water by mixing the stream of molten asphalt and the clay slurry continuously in a mechanical mixer. Among the special features in the control of the product is the selection of the proper kind of clay and the control of the hydrogen-ion concentration of the suspending agent. Bentonite has been found satisfactory as a suspending agent.

Morrell [85] describes a process for the production of bituminous and asphaltic suspensions and emulsions or the like, which consists in preparing and adding to an emulsion of an oleaginous material a suspension of a non-fluid pitchy, asphaltic or bituminous material which results in a stable emulsion after coalescence of the non-fluid particles of the suspension with the oily globules of the emulsion. Various protective colloids and emulsifying agents are cited, which includes the proteins, pectins, polysacchrides, hemicelluloses, gums, soaps, tannins, clays and mixtures thereof.

Homogenization of Cracked Residual Oils

One of the problems encountered in the early history of cracking was the formation of suspended carbonaceous or pitchy material in the residual oils resulting from cracking the relatively high-boiling hydrocarbon fractions of petroleum for the production of relatively low-boiling hydrocarbons suitable for motor fuel. Owing to the improvements in operation of the cracking process by the introduction of the non-residuum cracking and flashing operations, this problem has been largely eliminated but it may be successfully solved by methods which are in the realm of colloid chemistry.

The processes [86] for accomplishing this generally include subjecting the residual hydrocarbon oils containing suspended carbonaceous or pitchy material to homogenization by means well known at present, such as forcing the oil under pressure through small apertures or otherwise subjecting the suspended particles to a strain to cause the breaking up of the larger particles into smaller particles in the so-called colloid mill. In some instances, stabilizing agents, usually of a colloid nature and soluble in the oil, for instance, soaps of the alkaline earths such as the oleates, stearates, palmitates, resinates of calcium and magnesium, and the like, are added to the oil.

One of the most practical applications of the above-mentioned method and process [87] is disclosed, wherein the suspended pitchy and carbonaceous particles are concentrated together with accompanying liquid by settling to a mass of a paste or mud-like consistency and thereafter homogenizing the said concentrate. The settled supernatant oil is disposed of in the usual way.

The original material has a more or less grainy appearance tending to settle and agglomerate into a hard coke-like mass on standing. A creamy suspension of more or less pasty consistency of an extremely smooth appearance and feel when subjected to rubbing between the fingers is produced. The material may be blended with fuel oils so as to permit easy pumping through fuel lines. The original untreated material when stored in tanks hardens to a coke-like mass which represents not only an economic waste but is costly to remove and dispose of. The treated material does not agglomerate or settle out and such settling as occurs is easily reversed by mild agitation.

The following are some of the results obtained by the above-mentioned process:

Color, Gums and Resins in Petroleum Products

It is likely that the coloring matter in oil is present both in molecular and colloidal form as there are all stages of color formation from the practically colorless parent material through the intermediate stages to the final colored product which may consist of a true solution or of a colloidal dispersion and which in some cases separates into distinct layers.

Brooks and Parker [88] suggest that the bright yellow color of freshly dis-

	A: Residue from Mid-Continent Cracked Residuum Untreated	A: Treated Mill Type 1	A: Treated Mill Type 2	B: Residue from California Untreated Cracked Residuum	B: Treated Mill Type 1	B: Treated Mill Type 2
Specific gravity	1.033	1.072	1.024	1.028	1.030	1.0147
A. P. I. gravity	5.5	0.3	6.6	6.1	5.9	7.9
Per cent B. S. (solid matter)	80	65	52	80	60	42
Per cent settling at room temperature (standing)	Agglomeration grainy appearance	None	None	Agglomeration grainy appearance	None	None
Accelerated settling at 220° F.	Settled to solid	None	10%	Settled to solid	None	10%
Per cent water	1.5	2.5	2.5	1.8	3.5	4.0
Distillation						
I. B. P.	357	402	415	465	415	375
E. P.	700	735	710	712	745	710
Range	343	333	295	247	330	335
Per cent over						
5	410	470	480	510	440	445
10	515	536	506	525	512	500
15	545	570	570	575	568	560
20	565	598	591	603	615	602
25	585	625	625	635	643	630
30	610	655	656	650	665	652
35	645	681	675	675	695	662
40	675	702	682	668	715	682
45	690	708	692	675	725	675
50	695	725	675	638	734	710
55	700	735	685	582	742	706
60	675	731	687	62% over	745	685
65	665	720	710		715	690
70	645	70% over	660		690	700
75	73% over		74% over		73% over	78% over
80			660			
85						
90						
95						
Coke per cent (by wt.) after distillation	26.7	35.2	29.7	38.0	31.5	25.2

tilled cracked gasoline may be due to diolefins with conjugated bonds such as the fulvenes, the best known of the conjugated dienes.

Carpenter [39] believes that color formation is due to unstable resin-forming bodies of the cyclic pentadiene group.

Brooks [40] states that it is improbable that the coloring matter in petroleum distillates are hydrocarbons since there are but few colored hydrocarbons known. He also points out that fluorescence may be due to particles of sulfur, tar or other substances in a colloidal state of dispersion.

Brooks [41] in an earlier publication also ascribes fluorescence in distillates to benzenoid-like hydrocarbons, pointing out that oils distilled *in vacuo* are much less fluorescent than those distilled under atmospheric conditions, also that no fluorescent organic substances are known which belong to the paraffin or naphthene series of hydrocarbons and further that the vast majority of organic substances known possess condensed ring structures of benzenoid characteristics, also that the fluorescent substances when sulfonated react like the benzenoid hydrocarbon.

Exposure of cracked hydrocarbons to sunlight or artificial actinic rays or ultra-violet light, especially in the presence of oxygen, speeds up the formation of colored bodies although polymerization may occur in the dark and in the absence of oxygen.

Gums.

Gummy or resinous deposits formed upon evaporation of light distillates are generally referred to in petroleum technology as gums. These gum- or resin-like substances present one of the most important and interesting problems in the petroleum refining industry. Smith and Cooke [42] postulate the necessity of the presence of aldehydes, particularly formaldehyde, for the formation of gums.

Brooks [43] disagrees with the conclusions of Smith and Cooke in regard to mechanism of gum formation and finds that the addition of formaldehyde does not increase the gum. Brooks postulates the formation first of organic peroxides from the unsaturated hydrocarbons which in turn break up to form aldehydes and other oxidation products.

Vorhees and Esinger [44] found that when oxygen is passed into gasoline an induction period occurs first, after which the oxidation rate increases and the rate of gum formation greatly increases. They differentiate between actual gum and potential gum, the latter being the parent material which causes gum formation under favorable conditions for the same.

Likewise, Wagner and Hyman [45] differentiate between pseudo gum and true or residual gum. The pseudo gum may be formed on exposure to light, oxidation and other conditions, whereas the true gums are formed on evaporation to dryness. They also postulate an induction period in the formation of gum by oxidation during which intermediate products are made which catalyze the formation of gum.

Egloff, Faragher and Morrell [46] studied the effect of inhibitors and checking the formation of gum and color compounds in gasoline as well as the depreciation of knock rating resulting from storage and oxidation changes. A great many substances were found which inhibited the formation of gum and color as well as the depreciation in knock rating. Various methods were described for restoring gasolines which had been subjected to severe oxidation conditions to their normal values in regard to color, gum and antiknock value. Reducing agents such as sulfites, stannous chloride, acid and zinc were found particularly effective in the restoration process.

Gums and resins from cracked distillates.

J. C. Morrell[47] prepared resinous bodies suitable for varnishes and useful for the manufacture of protective and decorative coatings. The resins were recovered from cracked distillates by treating them with adsorbing agents either directly or by passing the vapors through the adsorbing agents or by distilling the distillate over the adsorbent material, and subsequently extracting the resinous materials from the adsorbent material with organic solvents such as alcohol, ether or mixtures. The solution is then evaporated leaving the resinous material. Various adsorbents such as fuller's earth, bentonite and other clays, charcoal and similar materials have been used.

Resinous bodies so recovered may be further treated[48] for the production of suitable surfacing material or for other uses, by subjecting them to the action of oxidizing agents such as air, oxygen, ozone, or to the action of polymerizing agents such as the salts of the heavy metals, for example ferric chloride, zinc chloride, stannic chloride, producing in general the hard, resin-like bodies desirable in many industrial applications.

Miscellaneous Products

Among the miscellaneous petroleum products which may be classed as colloidal in character are detergent soaps; cutting oils and insecticides which are generally of an emulsion character; emulsifiable cutting oils, which are water soluble and contain as emulsifying agents, phenolates, sulfonates, castor oil or soaps, and are used for the lubrication of metal cutting tools. Soaps with a petroleum base are made by dispersing mineral oil in a mixture of water and soap. These soaps which have "semi-solid" consistency, combine the detergent action of ordinary soaps with the solvent action of oils. They produce a lather which is very effective in removing oil.

Oil emulsions find employment as insecticides. Oil alone cannot be applied to plants, as it would kill them and would be too costly. Satisfactory results are obtained by using emulsions containing 0.5 per cent to 0.2 per cent of oil in water. Soaps and soap solutions are employed as emulsifying agents. Oil emulsions are also used for the softening of threads in textile spinning.

Petrolatum (petroleum jelly or vaseline) appears to be an emulsion of soft paraffins dispersed in oils. Various artificial jellies similar to the natural product are compounded of solid paraffin and heavy oils, but they do not possess the salve-like characteristics of the natural product, having a tendency to deposit solid matter when cooled, analogous to the crystallization of ice from ice cream, in the absence of a protective colloid such as gelatin.

Acheson's oil-dag and aqua-dag are examples of colloid dispersions. The oil-dag contains approximately 15 per cent of so-called deflocculated graphite. When oil-dag is diluted with benzene, electrolytes and adsorbent agents may be used to remove the suspended graphite.

Colloidal fuels * consisting of pulverized coal suspended in oil have been used to some extent by the United States Navy Department. A protective agent or fixateur is used to stabilize the particles of pulverized coal dispersed in the oil. According to a description from United States Navy Department, pulverized coal can now be successfully held in suspension so that the colloidal liquid flows freely through the pipes, preheaters, and burners of ships and power, heating, and industrial plants equipped to burn fuel oil. Months after mixing, the composites show little or no deposits. A fixateur, which comprises about 1 per cent, or 20 pounds per ton, acts to stabilize the particles

* *See* paper by L. W. Bates in this volume. J. A.

of pulverized coal dispersed in the oil. Fuels of this kind are said to show promise for further development and use.

It is believed that much further study of a precise experimental nature is warranted to extend our knowledge of the colloidal aspects of the petroleum industry.

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Colloid Chemistry and Petroleum

By Prof. L. Gurwitsch, University of Baku.

One of the most important colloidal properties is optical inhomogeneity. So far as research has shown, up to the present, this property is only very poorly developed in petroleum oils. Upon Rakusin's suggestion,[1] Zsigmondy investigated a specimen of oil residuum from Baku (a residue remaining after distillation of the lubricating oil fractions) and found submicrons in it; the number of these was, however, very small and unimportant in comparison with the very pronounced strong fluorescence of the solution.

Also Schneider and Just [2] observed very few submicrons in a yellow mineral oil, and Holde [3] found no submicrons in yellow machine oils, but observed a continuous light cone; but since the light of this light cone is not polarized in decolorized (or resin-free) oils, and is only weakly polarized in unrefined oils, we have to do not with the scattering of light by colloid particles, but with fluorescence. The absence of, or only faintly evident, optical inhomogeneity is, however, no proof of the lack of colloidal character of these oils, since many true colloidal solutions appear homogeneous if the difference between the refractive indices of the dispersed and external phases is very small.

The property of first importance in true colloidal solutions is the ability to change their physical state, to form reversible or irreversible gels by the action of physical factors such as heat, or certain chemical reagents. This property also has not been definitely determined in the case of petroleum oils. Schulz [4] considers the action of sulfuric acid in refining to consist essentially in the "flocking out" of asphaltic matter; the results of Condrea's [5] and of my experiments [6] are not in accord with this conception and show that the formation of the so-called acid tar is essentially a chemical reaction.* The precipitation of asphaltic matter from mineral oils by petroleum ether is often regarded as a colloid gel formation, and as irreversible; it is to be remembered however that for such precipitations relatively large proportions of solvent are necessary so that we may have to do here with a case of ordinary precipitation as a result of a change in the solvent, such as also happens in solutions of crystalloid substances. Finally, Day's [7] suggestion that it should be possible to flock out colloid asphaltic matter by means of various electrolytes requires confirmation, since it is not impossible that in his preliminary experiments, which have not been further investigated, a chemical process or reaction had taken place, for example the formation of chemical double compounds (perhaps with sulfur derivatives). The author was unable to produce any precipitate of asphaltic matter from a crude oil from Balacheny on treating it with an ethereal solution of corrosive sublimate. Also Schulz observed no precipitate whatever on treating a kerosene distillate with a saturated solution of zinc chloride. It should be noted, however, that non-coagulation by electrolytes is no proof of the non-colloidal character of petroleum oils, since this property is dependent upon the interaction of electrical charges and these are always very weak in the case of organosols.

* But this chemical change must be followed by aggregation of something into particles which separate out. J. A.

The two properties which served originally to distinguish crystalline and colloidal substances has been only very meagerly investigated in the case of mineral oils, i.e. diffusion and osmosis, and also cataphoresis, which properties have been so useful in characterizing colloidal solutions. There are statements in the literature regarding the extreme slowness of diffusion of petroleum oils, for example, the slow intermixing of two oils on long standing in a storage tank. But when one remembers the great internal viscosity of the heavy mineral oils and heavier distillates, one cannot *a priori* consider that the slow diffusion is determined by the colloidal character of these oils and not by their high viscosity. Several preliminary experiments carried out by the author are more in accord with the latter idea, since after diluting with light benzine, lubricating oils and even part of the resinous substances diffuse with very considerable velocity. Also the osmosis of heavy mineral oils, diluted with benzine, through a parchment membrane, takes place rather rapidly. As regards cataphoresis, Brooks and Bacon [8] observed no cataphoretic effect in a solution of lubricating oil diluted with kerosene, under the influence of 3,000 volts.

From the foregoing one must conclude that the properties generally characteristic of the colloidal state are only very indefinitely developed in petroleum oils. But when we examine the solid and semi-solid asphaltic and resinous substances deposited from petroleum, these being strictly amorphous substances which take up small proportions of admixed mineral oil, and yield entirely homogeneous substances which gradually soften (on heating), etc., we must consider them as colloids in order to explain their behavior. The frequently expressed opinion that the higher boiling oils, freed from resinous and asphaltic material, are of colloidal character, appears to me to lack any foundation, in fact to be contradicted by many facts. According to Norman,[9] the mean molecular weight of an American cylinder oil was 660 and a similar oil from Russian petroleum only 465; naturally there are hydrocarbons in these oils of considerably higher molecular weight, but since the lowest boiling fractions of these oils do not boil below 320° C. and therefore contain no substances of smaller molecular weight than about 320 to 350, and though there are constituents present of molecular weight somewhat greater than 600 to 800, one cannot conclude from these molecular weight values that these oils possess colloid character.

The frequently expressed opinion that paraffin is present in crude oils in a colloidal condition and is only converted to the crystalline state by distillation, lacks, in my opinion, any experimental foundation. In fact I have found that all the paraffin base oils of widely different origin, which have been investigated (Tscheleken, Ssuzachany, Grosny, Rumania, Galicia, Pennsylvania, etc.) show an abundance of paraffin crystals when examined microscopically in polarized light.[10]

If we now turn to those phenomena which are caused by the colloidal character of certain petroleum constituents, we should note as most important the subject of oil emulsions. In most cases it is the amorphous resinous material, which, like most dissolved colloidal material, greatly depresses the surface tension at the oil—water interface, and according to the Gibbs rule, concentrates at the interfaces and in this way forms a protecting film about the water droplets. These films may be of different stability according to the nature of the petroleum, and give emulsions of varying character. In certain petroleum emulsions soaps of naphthenic acids, also in a colloidal condition, form such a protective film.[11] If then the formation of petroleum emulsions is dependent essentially upon the colloidal character of certain constituents,

the methods for the resolution of such emulsions (or their separation into water and oil) should be regarded as colloid-chemical or colloid-physical processes. The most important of these will be briefly described.

According to v. Pilot and Piokowsky[12] certain oil emulsions are quickly resolved by heating under pressure to about 130° to 135° C. This affects the emulsion in two ways. First, it greatly diminishes the viscosity of the oil, which greatly facilitates the movement or settling of the suspended water droplets. But generally the degree of dispersion of the dissolved colloidal material, in this case the asphaltic and resinous substances, increases with rising temperature and as this change goes on the tendency of these substances to form protective films is greatly reduced.

Another more important and more interesting method for the resolution of such emulsions is that in which a hydrophilic colloid, such as soap, glue and the like, are added. The resins and lime soaps of naphthenic acids, which form the protective films of most petroleum emulsions, belong to the class of hydrophobic colloids; this is the reason why, in accordance with Bancroft's principle, water forms the dispersed phase in most petroleum emulsions.[13] Clowes[14] showed that in the presence of both types of colloids,—hydrophilic and hydrophobic, in definite proportions, no protective film and consequently no stable emulsion can result. The addition of small proportions of soap or similar material accordingly destroys the film of the hydrophobic colloid of many petroleum emulsions and effects a relatively easy separation of the oil and water.[15]

In the refining of petroleum products we also have to do with colloid-chemical processes. The formation of the so-called acid tar in refining by sulfuric acid is essentially a chemical process; but this acid tar takes up a certain amount of the oil, and this is really a colloid phenomenon; in other words, a swelling of the colloidal resin by oil. Also, in acid refining an unstable combination of acid and resin, possibly of colloidal character, is formed which partially remains in the oil and slowly liberates acid on standing.[16]

In the alkali purification of petroleum products, the resulting soda soaps of the naphthenic acids tend to form emulsions. Since the protective film in this case consists of the hydrophilic soda soaps (and not the hydrophobic calcium soaps, as in the case of natural emulsions of crude oil), the oil forms the inner and the water the external phase, in accordance with Bancroft's principle. The colloidal character of the soap solution, and also the power of emulsification, increases with the molecular weight of the fatty acids,[17] and this is also the case in the naphthenic acid series; and, as a matter of fact, emulsions are formed with particular ease in the alkali refining of the higher petroleum fractions. On the other hand, Krafft[18] showed long ago that soaps in alcoholic or aqueous alcoholic solution are present in the monomolecular, not in colloidal condition. In direct agreement with this is the fact that in treating acid oils with aqueous alcoholic caustic soda (instead of aqueous caustic) no emulsions result, and that the emulsions formed in aqueous solutions are destroyed by the addition of alcohol. An interesting case of colloid phenomena is exhibited by this behavior. Aqueous solutions of naphthenic acid soaps (like other soap solutions generally) are able to take up considerable quantities of neutral oil, and this is not in an ordinary emulsified condition, but is in such a highly dispersed state that the solution is no less transparent than the original soap solution. But the most interesting fact in this connection is that the oil is most tenaciously held by the colloidal soap particles, so that on agitating such a mixture with benzine, only very small proportions of the oil are extracted. But on adding alcohol to such a solution, the colloidal

character of the solution is so greatly altered that the oil quickly coalesces to form a coarse unstable emulsion.*

Colloid chemical phenomena have to be dealt with in the study of the adsorption of petroleum. The colloidal asphaltic and resinous constituents are most readily adsorbed.[19] In comparing different oil fractions, or the resinous material separated from them, it is found that the material from the higher fractions, or those of higher molecular weight, are most readily adsorbed. Apparently unrefined oils containing resinous material are able to hold more paraffin in solution than refined oils; the latter therefore generally have a higher congealing point than the corresponding unrefined distillates; also paraffin separates from purified oils in notably larger crystals than from oils containing resinous or asphaltic matter.†

The adsorption of the colloidal petroleum resins or pitches can be effected by means other than by solid, porous materials. However, the observations bearing upon this point have at present no practical value but are of some theoretical interest. According to Neumann,[20] petroleum oils can be partially decolorized by agitating with certain aqueous dye solutions, when a portion of the coloring matter of the oil is adsorbed in the film at the interface of the two liquids. I have also observed the partial decolorizing of kerosene by adding small proportions of a colloidal metal, such as lead, and then agitating with solution of an electrolyte which precipitates the colloidal metal and the coagulated metal carries part of the coloring matter down with it.

Finally, when we turn to the manufactured petroleum products a few may be mentioned whose colloidal character is of particular interest. The solutions of fats or solutions of lime, soda or potash in mineral oils belong to this class and have been thoroughly investigated by Holde,[21] who showed their colloidal character. Also certain materials (such as caoutchouc, aluminum or heavy metal salts of fatty or naphthenic acids) employed to increase the viscosity of lubricating oils, may be classed as colloidal solutions. Acheson's "Oildag" should also be mentioned; this is an oleosol of specially prepared graphite, which has found a place for itself in the industries.‡

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[10] In this connection it is not intended to deny the possibility that colloidal paraffin or other colloidal substances may exist in petroleum; but it should be reiterated that we have no experimental evidence for such a theory.
[11] Cf. Gurwitsch, *Petroleum*, 1922, 1270.
[12] *Petroleum*, 13, 145.
[13] *J. Phys. Chem.*, 19, 275 (1915).
[14] *J. Phys. Chem.*, 24, 407 (1920).
[15] Cf. *J. Ind. Eng. Chem.*, 13, 1010 (1921).
[16] Gurwitsch, *Petroleum*, 1923.
[17] Donnan, *Z. physik. Chem.*, 1899, 31, 42.
[18] *Ber.*, 32, 1595 (1899).
[19] The suggestion of Rakusin that the soft paraffin in paraffin-base oils is more easily adsorbed than resinous matter, has been shown, by experiments in my laboratory (soon to be published), to be altogether incorrect.
[20] German Patent 266,034.
[21] *Kolloid-Z.*, 1908, 6.

* We have here a case of destruction of protective action by *too profound a degree of dispersion of the protector, soap.* Ferric chloride de-emulsifies gum arabic-oil emulsions, by *coagulating the protective gum.* J. A.

† Colloids profoundly affect the size, number and shape of crystals. See references in Vol. I of this series. Also J. Alexander, *Kolloid-Z.*, 1909. J. A.

‡ *See* paper by E. G. Acheson in this volume. J. A.

The "Free Carbon" of Coal-Tar

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Coal-tar is a viscous liquid of a black color when viewed in the mass and is obtained by the pyrolysis of coal. It varies in its physical properties and chemical constitution, depending upon the conditions under which it is formed and to which it is exposed before it is condensed in its liquid state. It is without doubt a combination of a solution and a suspension, the suspended particles being of various degrees of size from microscopic to ultramicroscopic dimensions. The chemical constitution of the soluble portion is of great scientific and economic importance but we are considering here only those bodies which can be isolated from coal-tar as insoluble materials obtained by treating coal-tar and its pitches by various so-called solvents.

Since coal-tar has already been in the vapor state during its formation, it should theoretically be capable of complete redistillation except for those non-volatile portions which may have been carried along by the coal gas and tar vapors by entrainment and materials such as the ash, which are largely made up of metallic compounds and result from the corrosion of pipe lines and containers used for storage and transport. Disregarding impurities such as coke dust and ash, we find that an important portion of the coal-tar is not redistillable without decomposition even under high vacuum and that the undistillable portion bears some relation to the so-called "free carbon" content of the tar. This latter characteristic is also linked in some way to pyrogenetic changes which take place in the carbonizing retort. That is, the higher the retort temperature and the longer the time of contact of the tar vapors with superheated surfaces, the greater will be the "free carbon" content of the resulting tar. Naturally, the gas retort tars contain more of this material than do other tars, one rather unusual specimen having been found to contain 38 per cent of "free carbon." Next in order come the coke oven tars, then the vertical retort tars and finally, the low temperature tars, which latter sometimes contain less than 0.2 per cent of "free carbon." The carburetted water gas and oil tars are also usually quite low in "free carbon" but these also vary according to the temperatures prevailing during their formation, and the kind of oil used for carburetting.

It is a matter of common knowledge that the amount of insoluble residue obtained on treating tars and pitches with various solvents varies widely—thus a greater amount of insoluble is obtained with paraffinic petroleum distillates than with any other common solvent. The work which has been done with petroleum solvents is unfortunately of little value, largely because the petroleum solvents vary among themselves in their action, depending on their boiling ranges and the nature of the contained hydrocarbons and thus far no standard petroleum hydrocarbon or mixture of hydrocarbons has been produced which is readily obtainable and duplicatable for such investigations.

"Free carbon" is defined by common usage in the United States as the insoluble material obtained from tar by treating it with benzol and toluol in

an empirical way. The usual method for its determination is that described by Weiss.[1] The term "free carbon" is a misnomer as the insoluble residue is not elemental carbon but is a material high in carbon, not very different in ultimate analysis from tar itself. The insoluble residue of the "free carbon" determination includes the mineral ash but since this is extraneous matter it is deducted in our consideration of the matter. Some tars, for example, blast furnace tars, contain amounts of ash some fifty to one hundred times that of ordinary coal tars and in such cases very serious errors enter if consideration of the ash is neglected.

A series of analyses made by Hubbard and Reeve[2] of the insoluble residue obtained by digesting tar with carbon bisulfide showed the following general results: Carbon, 90.17 to 94.26 per cent; hydrogen, 2.59 to 3.31 per cent; oxygen, 1.81 to 5.91 per cent; sulfur, 0.50 to 1.78 per cent; nitrogen, none by qualitative test.

The authors have made ultimate analyses of "free carbon," that is, the material insoluble in toluol and benzol as the solvent and the various results obtained fall within the following ranges after correcting for mineral ash:

	Maximum Per Cent	Minimum Per Cent		Maximum Per Cent	Minimum Per Cent
Carbon	91.7	90.0	Oxygen	3.3	2.5
Hydrogen	4.0	3.4	Sulfur	1.4	0.7
Nitrogen	1.2	1.0			

"Free carbon" has a specific gravity at 15/15° C. of 1.45 to 1.53 and an apparent density of 0.55 to 0.60. On heating in a closed crucible it partially fuses and coalesces somewhat but produces a very friable coke. It is evident that this constituent of tar and pitch is not responsible for the very strong, sharp coke which is produced by the destructive distillation of pitch in a bee-hive oven.

From past experience, "free carbon," as known in American practice, is considered to be an organic compound of high, though variable melting point and of great complexity.

Since practical results indicated that there was some general relation between the performance of tars and pitches for various types of construction work and the "free carbon" content determined by the empirical testing method, it has been held that the "free carbon" acting as a very finely divided filler suspended in the bitumen, was responsible for this relation. This rule does not always hold and it was decided to study the action of various solvents on tars, to investigate the insoluble as well as the soluble materials obtained therefrom and to attempt an interpretation of the practical results on the basis of such information. This correlation has not been finished but we hope that the information which is reported here can be used by other investigators in extending this work.

Monroe and Broderson[3] have attempted to show that tar forms compounds with chloroform which results in an increase of insoluble matter. They based their opinion on boiling point changes of the solution under investigation. In a similar way they conclude that benzene and carbon bisulfide do not form such compounds. An examination of their experimental results, however, strongly indicates that the probable errors of measurement are such that the conclusions are questionable. Further, they have assumed that all compound formation results in insoluble material. It is not unreasonable to suppose that some of the compounds formed with various solvents are soluble, and on this basis, their results can be interpreted to give very different conclusions.

Later Hodurek [4] has published a very extensive study of the "free carbon" of European tars, in which he reviews many of the methods which have been proposed for "free carbon" determination. He states that tar contains certain insoluble material which can be removed by filtration and which he designates as "Carbon I." He also found that other material, "Carbon II," is formed by precipitation from the tar through the action of certain solvents of which he mentions ethyl alcohol, methyl alcohol, petroleum benzine, benzol, toluol, xylol, pyridine, ether, acetone and glacial acetic acid. On the other hand, he states that aniline, quinoline, phenol, cresol, nitrobenzol, naphthalene oil, anthracene oil and heavy oil of brown-coal tar do not cause this precipitation of "Carbon II." These conclusions were reached by the microscopic examination of filtered tar followed by the addition of the various solvents on the slide during observation. He further shows that the amount of "Carbon II" obtained is dependent on the solvent used, while the "Carbon I" is independent of the solvent. He gives tests of 25 tars varying from 1.86 to 12.4 per cent total insoluble in benzol which show from 1.38 to 6.70 per cent "Carbon I" with this solvent and from 0.39 to 5.7 per cent of "Carbon I." The amount of "Carbon II" is always greater than "Carbon I" but the relative amounts vary between 1.06 to 1 minimum and 94 to 1 maximum. His further study of the distillation of tars to pitches indicated that in the earlier stages of distillation until about 50 per cent of oils are distilled, the absolute amount of "Carbon I" remains constant while "Carbon II" shows a continued rise. Later in the distillation where strong decomposition is evident, the "Carbon I" rises rapidly while "Carbon II" reaches a maximum and then falls off to approach the condition of coke and total insolubility. Our experience with the distillation of American tars has largely duplicated Hodurek's findings.

The work of Hodurek is of great interest but in the authors' opinion his selection of the matter insoluble in anthracene oil does not represent the ultimate insoluble matter of the tar. Experimental results on this point will later be presented.

A portion of the original results presented in this chapter has already been published by one of the authors,[5] but much of what is given there will be of necessity repeated in order to present a complete picture of the information available. The earliest experiments dealt with chloroform as a solvent in the attempt to produce a tar free from insoluble matter. The tar selected was a coke oven tar containing about 5 per cent of "free carbon" as determined with benzol and toluol according to the method described by Weiss (*loc. cit.*).

Experimental.

A weighed quantity of tar (about 500 grams) was mixed with about ten times its volume of warm pure chloroform and the solution filtered twice through weighed thimbles made of two thicknesses of S. & S. No. 575 hardened filter paper. When all soluble material had passed through the thimbles, these were placed in extractors and exhausted with hot chloroform in place of benzol as used in the "free carbon" analytical method. The chloroform solutions were refiltered through fresh thimbles and the resulting insoluble materials again extracted with chloroform. All the thimbles were dried to constant weight at 100° C. The combined filtrates and washings were brought into a tared flask connected to a condenser and the bulk of the chloroform distilled off on a steam bath. The condenser was then disconnected and the bituminous material was held at a temperature of 80° C. until it had regained its original weight, less the amount of insoluble matter removed. This latter amounted to 5.54 per cent. At this point all odor of chloroform had completely disappeared.

This supposedly carbon-free tar was then tested by the toluol-benzol method and also by a chloroform extraction to determine the percentage of insoluble matter. We refer to

this as "treated tar" and this term will be used to designate the material soluble in a solvent after the latter has been removed. The results were:

	Original Tar	Chloroform-treated Tar
	Per Cent	
Insoluble in		
Toluol and benzol ("free carbon")	5.50	10.05
Chloroform	5.36	0.88

Apparently, chloroform forms a compound with the tar which is insoluble in benzol but substantially soluble in chloroform, a contingency that was apparently not considered by Monroe and Broderson. This benzol-insoluble material is quite different in appearance from ordinary "free carbon." The latter is dull black, while this substance has considerable luster and can be sintered together by careful heating. Under the microscope it appears partially crystalline. No quantitative test for chlorine was made on this substance but on oxidation with fuming nitric acid, a very strong qualitative test for chlorine was obtained in the resulting solution.

Following this, a similar amount of the same original tar was treated in like manner, using pure benzene as the solvent instead of chloroform. The tests of this treated tar were:

	Original Tar	Benzene-treated Tar
	Per Cent	
Insoluble in		
Toluol and benzol	5.54	4.71
Chloroform	5.36	2.17

The residues obtained from this treated tar also did not resemble ordinary "free carbon," being brown instead of black. Under the microscope the appearance was amorphous. On heating, it sintered, forming a good coke.

Hanging drops of the original tar and of the tars after treatment with chloroform and benzol respectively were examined on microscope slides under a magnification of 87 diameters. The two treated tars appeared homogeneous and clear red-brown in color. The untreated tars showed numerous black grains of various sizes over the same red-brown ground. When a drop of the chloroform-treated tar was mixed with a drop of chloroform on a slide, the homogeneous character remained unchanged, while if a drop of benzol was added to the chloroform solution, granules appeared. The benzol-treated tar mixed similarly on the slide with benzol became granular and slightly crystalline and with chloroform likewise showed grains and some fine needle-like crystals.

The results are tabulated as follows:

Slide No.	Material	Appearance
1	Original tar.	Very granular with amorphous grains of various sizes.
2	Tar resulting from chloroform treatment.	Clear, without grains.
3	Tar resulting from benzol treatment.	Clear, without grains.
4	Mixture of No. 1 and benzol.	Strongly granular.
5	Mixture of No. 1 and chloroform.	Strongly granular.
6	Mixture of No. 2 and benzol.	Very strongly granular.
7	Mixture of No. 2 and chloroform.	Nearly clear.
8	Mixture of No. 3 and benzol.	Granular and slightly crystalline.
9	Mixture of No. 3 and chloroform.	Granular and fine, needle-like crystals.

The results indicate that both chloroform and benzol in contact with tar either form insoluble bodies with some of the tar constituents or break a col-

loid suspension present in the original tar. If compound formation takes place, the compounds are at least partly insoluble in benzol, and to a lesser degree, in chloroform.

In the light of the foregoing results, experiments were then instituted to see whether "free carbon" would increase with the time the solvent and tar were allowed to remain in contact in the cold. The same original tar was used for this work as in the previous experiments. Except for the time of standing with the first amount of solvent added, the general procedure in all cases was identical. In one series of tests, toluol was used as the contact solvent; in another, benzol.

Time of Standing Hours	Insoluble in Benzol Per Cent	Insoluble in Toluol and Benzol Per Cent
0.25	6.42	5.54
24	6.65	6.30
90	7.74	7.55
138	9.25	8.44
258	10.72	9.34

The longer the tar stands in contact with the solvent, the greater is the amount of insoluble residue obtained. This steady rate of increase was continuing at the end of the test. The reaction is evidently accelerated by the presence of a large excess of the solvent and occurs practically equally with benzol and toluol.

With only small amounts of benzol present, such as are naturally in an ordinary tar, it seemed conceivable that this reaction might take place even if at a very low velocity. In other words, with long time the amount of apparent insoluble matter in a tar might progressively increase. This assumption was not borne out by our observations made on tar which had stood for a period of two years.

Experiments were then instituted to see whether carbon bisulfide and chloroform would give similar results. Tests similar to those with benzol and toluol were made, using cold carbon bisulfide and chloroform separately in contact with the tar. The following results were obtained on the same standard tar.

Time of Standing Hours	Insoluble in Chloroform Per Cent	Insoluble in Carbon Bisulfide Per Cent
0.25	5.91	5.84
48	6.93	6.62
120	8.27	7.37
216	8.01	7.67
288	8.21	7.52

A similar increase in apparent insoluble matter was noted here as with benzol and toluol, though at a lesser cumulative rate and the amount apparently reaches an ultimate maximum.

The insoluble residues from the chloroform extraction were tested qualitatively for chlorine with positive results but quantitative determination was not attempted. The residues from the carbon bisulfide extractions were assayed for sulfur by the "Eschka" method, the following figures being obtained:

	Time of Standing Hours	Sulfur Per Cent
Residue from a		
Benzol extraction	—	0.92
Carbon bisulfide extraction	0.25	1.46
Carbon bisulfide extraction	120	1.82

The general indication is that the solvent combines with some constituent of the tar although the results could also be explained on the basis that the coagulated carbon, when precipitated, adsorbs solvent which is not removed on drying in a steam oven.

A similar observation with carbon bisulfide was made by Hubbard and Reeve.[6]

Due to the fact that both CS_2 and $CHCl_3$ continue to precipitate insoluble matter from tar the search was continued to find a solvent without this action.

A series of experiments on various tars and pitches was made, comparing aniline and toluol as the contact solvents and using benzol afterward in the extractor.

	Insoluble Residue with Aniline Per Cent		Insoluble Residue with Toluol Per Cent	
Time of digestion	0.25 hour	72 hours	0.25 hour	72 hours
Coal-tar No. 1	3.22	3.71	5.09	5.31
Coal-tar No. 2	12.48	12.83	14.28	17.59
Coal-tar pitch	8.68	9.08	13.22	15.15
Water gas tar	0.02	0.17	0.02	0.19

Several tar residuals were tested at 0.25 hour only, using aniline versus toluol:

	Insoluble Residue with Aniline Per Cent	Insoluble Residue with Toluol Per Cent
Water gas tar pitch	4.11	5.28
Coal-tar roofing pitch	20.51	25.57
Coal-tar briquet pitch	17.30	21.13
Coal-tar paving pitch	13.08	16.72
Road compound	11.88	13.95

Various filtrates from this last set of tests were examined under the microscope by the hanging-drop method. With both aniline and toluol the first few drops filtered showed a very faint trace of insoluble matter; the remainder of the filtrate was in both cases perfectly clear when examined immediately. The aniline filtrate remained clear even after twenty-four hours' standing but the toluol filtrates showed an immediate and gradually increasing formation of insoluble matter in the form of amorphous grains. The formation of precipitate in the toluol drop was accelerated by further dilution with either toluol or benzol. The aniline solutions, similarly diluted with benzol or toluol, also showed precipitation but of a quite different nature, being in the form of clear, fine, crystalline needles.

These results are of the same general nature as those with the first tar investigated. In water gas tar products, where the insoluble residue is very small, the differences between toluol and aniline are not marked. Tar No. 1, which shows no increase on standing with toluol, was unusually high in tar acids and this fact may be the cause of its different behavior, as experience has shown that the addition of tar acids decreases the tendency to precipitation of insoluble matter by toluol and benzol.

The aniline and toluene filtrates of tar were examined under the ultramicroscope. The toluene solutions showed no evidence of motile particles while the aniline solutions showed a rich field of particles having characteristic Brownian movement. When benzol or toluol were added to the aniline solution, the motile particles were observed to lose their motility and they then were visible under the microscope.

Some recent experiments have shown that selenium oxychloride has a very much greater solvent action than aniline. Selenium oxychloride solutions of tar are very difficult to filter but can be handled with reasonable success by means of alundum thimbles, thereby obtaining filtrates which are optically clear when examined under the ultramicroscope. The insoluble matter contains adsorbed solvent which can be partially removed by washing with 25 per cent nitric acid. Two samples of the material insoluble in selenium oxychloride (1) from coke oven tar pitch and (2) from gas house tar, were submitted to ultimate analysis after drying at 105° to 110° C. The results, corrected for water (at 175° C.) and ash were:

	1	2
	Per Cent	
Hydrogen	2.0	2.2
Carbon	87.4	88.5
Chlorine	4.8	3.7
Sulfur	0.6	1.1
	94.8	95.5

If the chlorine present is assumed to be equivalent to the adsorbed selenium oxychloride, it accounts for somewhat more than the difference between the totals of the analysis and 100 per cent and would indicate roughly that the carbon held from $\frac{1}{9}$ to $\frac{1}{11}$ of its weight of selenium oxychloride.

The ratio of carbon to hydrogen is about 42 to 1 in the selenium oxychloride residues while residues from benzol treatment average 25 to 1. The results obtained by Hubbard and Reeve on carbon bisulfide residues average around 32 to 1. This shows that the material insoluble in selenium oxychloride contains less hydrocarbons than any other residue investigated.

The matter insoluble in selenium oxychloride is a black amorphous cake which readily breaks up to a very fine powder. On ignition to redness in the absence of air, no tendency to sinter is evidenced.

The effect of selenium oxychloride is shown compared with toluol-benzol and aniline in the following table:

	Insoluble in Toluol and Benzol ("Free Carbon")	Insoluble in Aniline	Insoluble in Selenium Oxychloride
		Per Cent	
1. Tar (coke oven)	6.4	4.6	3.6
2. Coke oven tar pitch, m.p. 300° F.	39.4	33.3	6.0
3. Coke oven tar pitch, m.p. 300° F.	27.9	19.4	7.8
4. Tar (gas house)	25.7	23.9	23.6
5. Gas house tar pitch, m.p. 151° F.	34.5	30.3	28.6
6. Tar (water gas)	3.4	1.6	trace
7. Water gas tar pitch, m.p. 100° F.	9.2	6.4	3.7
8. Vertical retort tar pitch, m.p. 100° F.	7.2	2.3	1.2

These tests are typical and it is evident that the gas house tars are much richer in real carbon in proportion to their benzol-toluol insoluble than any other type. On one pitch (No. 2) a test for Carbon I was run by the Hodurek method (*loc. cit.*) and a result of 12.2 per cent obtained, indicating that from a solvent standpoint, selenium oxychloride is the material which dissolves the greatest portion of the complex hydrocarbon mixture known as "free carbon". The fact that the solutions are optically clear when examined under the ultramicroscope disposes of the conclusion that the lower results are due to a peptizing action of the selenium oxychloride.

To summarize our knowledge of the situation, it seems to be established beyond doubt that "free carbon" is largely, if not entirely, composed of complex carbon-containing compounds.

Different solvents used to determine insoluble matter give different results and these varying results may be attributed to several physical effects:

1. Absolute differences in true solvent power.
2. Ability of the solvent to retain otherwise insoluble material in colloidal suspension.
3. (a) Combination of the solvent with tar constituents, and/or
   (b) adsorption of solvent by the insoluble matter, and/or
   (c) a coagulating action of the solvent on matter colloidally suspended in tar.

The second cause is evidently present in aniline solutions which show the presence of colloidal particles although optically clear by ordinary microscopic methods. As benzol, toluol and selenium oxychloride solutions were the only other ones examined by ultramicroscopic methods, we do not know whether other materials, such as pyridine, tar acids, carbon bisulfide and chloroform, give this effect.

Adsorption of solvent probably exists in all cases and in some such as benzol, toluol, carbon bisulfide and chloroform, there is certainly either a compound formation or a coagulation of colloidally suspended material. The authors incline to the former view because of the long time necessary to reach the limit of increase of insoluble matter in the case of benzol and toluol combined with the fact that freshly prepared solutions do not show Brownian movement.

The importance of knowledge concerning the suspended and colloidal constituents of tar is great and a systematic study of the problem using ultramicroscopic methods in all cases is much to be desired. It is hoped that such results can throw some light upon the susceptibility of tars, and particularly pitches, to changes in temperature.

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Asphalt

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The terms *asphalt,* of Babylonian origin, and *bitumen,* probably from Sanskrit, have been used during some thousands of years for natural products, mixtures of pitch-like substances and inorganic material. Modern chemistry adopted these terms, but much confusion arose regarding the import of these words. In some countries the name bitumen was given to that part of these natural pitch-like products which is organic, fusible and soluble in carbon disulfide, while in others the word bitumen had a more general sense, including mineral oils, natural gaseous hydrocarbons, etc., the word asphalt being applied to the dark-colored solid or viscous bitumens. The term asphalt was sometimes used only for products containing inorganic material, sometimes for products containing no mineral matter at all. Coal tar in some countries is considered as a bituminous product; in others it is not.

In order to put an end to the confusion, an international committee, "Comité pour la nomenclature et les essais" of the "Association Internationale Permanente des Congrès de la Route," solved the question in the following way. The term *bitumen* is used as a general name for a class of bodies which are closely connected to the mineral oils and coal tars. According to this definition, bitumens are mixtures of native or pyrogenous hydrocarbons and their non-metallic derivatives of a gaseous, liquid, viscous or solid nature and which are totally soluble in carbon disulfide.

The term *asphaltic bitumen* is given to those products which are called asphalt in one country and bitumen in others. It is a species of bitumen, native or prepared from native bitumen, with characteristic binding properties, being viscous or solid and containing little volatile material.

Asphalt is a native or artificial product, containing asphaltic bitumen mixed with inert mineral matter.

This nomenclature, although not yet generally accepted, will be followed here.

The genesis of the native asphalts is not very clear, but in many cases mineral oils must have been oxidized or sulfurized and mixed with mineral and organic substances. The organic part of these mixtures which is soluble in carbon disulfide, asphaltic bitumen, may be prepared artificially from certain mineral oils, so called asphalt-base oils, by distillation or oxidation. When artificial asphaltic bitumens are mixed with mineral products, such as sand, broken stone, powdered limestone, etc., artificial asphalts are obtained, which are of great technical importance, the production of native asphalts being by far insufficient to cover the world consumption. The great extension of the asphalt industry during the last decennia, is principally due to these artificial products.

The first exhaustive treatise on the chemistry of asphalt appeared in 1837 by J. B. Boussingault.[1] He separated the oily compounds (pétrolène) from the asphaltic substances (asphaltène), and supposed a simple relation to exist

between asphaltène and pétrolène, the asphaltènes being oxidation products of the pétrolènes. This hypothesis afterwards supplemented by the theory that the asphaltènes were oxidized or sulfurized pétrolènes,[2] proved to be incorrect, but his asphaltène-pétrolène system still exists in recent colloid chemical work on this subject as micelle-medium. After Boussingault, slow progress was made, the purely organic work giving little satisfaction. In the beginning of the twentieth century Clifford Richardson[3] published his researches on Trinidad asphalt. The same investigator had also already discovered the "carbenes"[4] in some asphaltic bitumens. His principal merit is the introduction of the ultramicroscope into this field of science. His ultramicroscopical researches were continued by E. C. Lord[5] and others. The first elaborate colloid-chemical investigation on asphaltic bitumen was published in 1923 by F. J. Nellensteyn.[6]

The Constitution of Asphaltic Bitumen.

Asphaltic bitumen belongs to the protected lyophobe sols. As such it contains three principal groups of components:

1. The medium,
2. A lyophile part: the protective bodies,
3. A lyophobe part: the ultramicrons.

The medium may be characterized as a mineral lubricating oil, consisting principally of hydrocarbons.

The protective bodies generally are highly unsaturated hydrocarbons, often with a high sulfur or oxygen content. In their physical properties these bodies may be best compared with resins. Otherwise little is known about their chemical composition.

The ultramicrons are particles of elementary carbon. A 1 per cent solution of asphaltic bitumen in carbon disulfide shows these particles by means of the cardioid ultramicroscope very clearly, although this image is not so easily obtained as with the natural asphalts. The ultramicrons may be oxidized by $KMnO_4$, forming mellitic acid and aliphatic organic acids. The mellitic acid represents the cyclic carbon, the aliphatic acids the non-cyclic aliphatic carbon. The mellitic acid is always found only in small quantities in the oxidation product; the greater part of the carbon seems to be non-cyclic.

Between the ultramicrons and the protective bodies there exists an adsorptive relation. It is most probable, however, that in these complicated products the hydrocarbons are dissociated and that these dissociation products are adsorbed in the same way as ions are adsorbed in hydrosols.

Stability Conditions.

In the system which is formed by the medium, the protective bodies and the ultramicrons, the disperse phase consists of the two last groups, these being the constituents of the asphalt micelles. The stability of the whole system in the first place depends upon the relation between the micelles and the medium. Changes in this stability, which are known as flocculative and peptizing reactions, give rise to a *"reversible flocculation."* If, however, the micelle itself is destroyed, the micelles cannot be repeptized, at least not directly. In this case we have an *"irreversible flocculation."*

The Reversible Flocculation of the Disperse Phase of Asphaltic Bitumen.

Upon adding benzene of low boiling point, ether, hexane, ethyl-acetate, etc., to a solution of asphaltic bitumen in CS_2, C_6H_6, etc., a precipitate is

formed. Apparently a new phase is formed, but this is not the case, for the asphaltic-bitumen solution itself is already a two-phase system, as is revealed by the ultramicroscope. This precipitation is simply due to agglomeration of the particles of the disperse phase; it is characterized by changes in the interfacial layers. The precipitate is called "asphaltènes," a name already introduced by Boussingault (1837). It represents the asphaltic bitumen micelles in a more or less pure state. So this asphaltène reaction may give an idea of the quantitative relation between micelle and medium in these systems.

The precipitation of the asphaltènes in many respects may be compared with the breaking of an emulsion. Although in the disperse phase the asphaltic bitumen micelle contains elementary carbon, asphaltic bitumen has a more emulsoid character, the suspension properties being hidden by the protective bodies, as is often the case with highly protected lyophobe sols. A consequence of these considerations is that the stability conditions of "macro" emulsions may furnish useful data about the factors which rule the peptizing and flocculating conditions of asphaltic bitumen solutions, which may be considered as "micro" emulsions. The extensively investigated oil-in-water emulsions are of great importance in this respect. For these emulsions the stability depends upon: [7]

a. the electrical charge of the particles,
b. the conductivity of the disperse phase,
c. the interfacial tension,
d. the presence of solid protective layers enclosing the particles of the disperse phase.

It seems probable that for organosols conditions *a, b* and *d* are not of much importance, but that the interfacial tension especially determines the stability of the asphaltic bitumen solutions. An increase of the interfacial tension decreases the stability. Perhaps the solvation of the protective bodies, according to the theories of Kruyt,[8] also plays a part, but in any case the interfacial tension seems to be the first and most important stability condition. The amount of this tension is unknown, but it may be calculated with some restrictions, given by Antonow,[9] as the difference of the surface tension of both phases. Thus by adding a liquid which changes the surface tension of the medium, the interfacial tension micelle-medium is also changed. If σ_{f_1g} and σ_{f_2g} are the surface tensions of both phases, the interfacial tension $\sigma_{f_1f_2} = \sigma_{f_1g} - \sigma_{f_2g}$. Decreasing σ_{f_2g} causes an increasing of $\sigma_{f_1f_2}$. This occurs when flocculating an asphaltic bitumen solution; the flocculating reagents have a low surface tension and accordingly the asphaltic bitumen micelle has a high surface tension. Ranging various liquids which are miscible with the medium of asphaltic bitumen according to their surface tension, it is evident that all liquids with low surface tension are flocculating reagents, whereas those possessing a high surface tension are peptizing reagents.[10]

	σ 20° (dyne/cm.)	
Ether	17.1	Flocculating reagents
Benzene 40°–60°	17.4	
n-Hexane	17.4	
Ethylacetate	22.9	
Acetone	23.1	
Butanone	23.6	
Carbon Tetrachloride	25.7	Intermediate zone
Cyclo-hexane	26.0	
Chloroform	26.9	Peptizing reagents
Benzene	28.8	
Carbon Disulfide	31.0	
Pyridine	35.5	

Carbon tetrachloride (CCl_4) and cyclo-hexane (C_6H_{12}) show a surface tension which holds the balance between the values for the flocculating and the peptizing reagents. By this intermediate position these liquids may combine peptizing and flocculating properties. They are apt to flocculate especially when a less stable system has been formed. In practice this is caused by faults during distillation or blowing, or when road asphalt has been overheated during the melting process. A slight decomposition of the micelle when "free carbon" has not yet been formed, may be detected by adding carbon tetrachloride. This fact has already been stated by C. Richardson,[11] but according to the general classic organic views, he supposed the presence of special compounds, insoluble in carbon tetrachloride but soluble in carbon disulfide, which he called "carbenes" and which should always indicate an inferior character of the asphaltic bitumen. According to the preceding consideration, the intermediate position of carbon tetrachloride as *shown by its surface tension explains Richardson's reaction on the so-called carbenes simply as a reaction on a less stable asphalt micelle.*

Liquids showing high surface tension are also widely different in their peptizing properties. Generally the higher the surface tension, the better the solvent power. For asphaltic bitumen itself the oily medium is the solvent for the micelles. Therefore a certain relation may be supposed to exist between the surface tension of the medium in asphaltic bitumen (and also of asphaltic bitumen itself) and that of the peptizing and flocculative reagents. Only a few determinations of the surface tension of asphaltic bitumen are available.[12]

	Softening Point (Ball and Ring) °C.	Surface Tension (σ)	
		Dyne/cm.	°C.
Mexican residual asphaltic bitumen.........	40	23.5	180
Mexican residual asphaltic bitumen.........	65	25.2	180
Mexican airblown asphaltic bitumen........	67	23.2	200
Mexican airblown asphaltic bitumen........	80	23.1	200
Borneo residual asphaltic bitumen...........	63	23.2	200

The values for the surface tensions at room temperature are unknown, but certainly higher than 30 dyne/cm. This surface tension does not coincide with the critical surface tension of 25 to 26 dyne/cm. for the solvents, which marks the boundary between the peptizing and flocculative reagents. The asphaltic bitumen system seems to be stable far below its own surface tension. Perhaps this difference can be ascribed to the possibility, that the surface tension of the medium is lower than that of the total system.

The difference between the value for the surface tension of various asphaltic bitumens seems to be very small, which explains the fact that for all those products the same liquids may be used as peptizing or flocculative reagents. In some allied systems however great differences are evident; especially the coal tars show a much higher surface tension. The consequence is, that liquids which are peptizing reagents for asphaltic bitumen may be flocculents for these coal tars. In the paragraph on allied systems (coal tar, etc.) we shall deal further with this important question.

Liquids showing low surface tension also show great differences in their flocculating properties. The precipitation is never complete; even with a great excess of benzene the finest and most protected micelles are not precipitated.

Only by adding liquids which are not totally miscible with the medium or the protective bodies of asphaltic bitumen may a complete precipitation be achieved. In this case however, a pure flocculation no longer occurs and the precipitate differs considerably from the flocculated carbon micelle, for it contains a larger portion of oily compounds derived from the medium and the protective bodies.

When precipitating with these liquids, e.g. dilute ethanol or acetone, we get a "soft asphalt" instead of the "hard asphalt" yielded by the benzine flocculation. From the preceding it follows, that the difference between these precipitates is not of a chemical nature, as has always been supposed by the classic organic chemistry. It is not a lower or higher degree of polymerization of the asphaltic bitumen which causes a greater or lesser degree of solubility, but it is simply the interfacial tension and miscibility of the flocculating agent with the oily constituents of asphaltic bitumen, which determines the nature of the precipitated mixture.

The Irreversible Flocculation of the Disperse Phase of Asphaltic Bitumen.

While the reversible flocculation of the disperse phase of asphaltic bitumen is a pure physical phenomenon, irreversible flocculation is mostly caused by chemical reaction, involving radical changes in the relation between the ultramicrons and the protective bodies. By these reactions the protective bodies are attacked and often carbonized. This means an increase of the carbon content, i.e. of the ultramicrons and a decrease of the protective bodies, causing a decreased stability and often a total destruction of the whole system. Although these reactions are of high interest from a theoretical and practical point of view, little is known about their nature.

A physical reaction, causing irreversible flocculation, is the exhaustive extraction of the asphaltenes with different liquids of successively increasing surface tension. This reaction is theoretically important; it demonstrates that the degree of protection of the ultramicrons determines the solubility of the micelle and not a hypothetical chemical difference between products of different solubility, for which all sorts of names have been invented (as asphaltenes, carbenes, carboids, α, β- and γ-asphalt, etc.).

Oxidation Reactions.

These reactions are of utmost importance for the practical applications of asphaltic bitumen. In most cases asphaltic bitumen has been formed by oxidation, but if the reaction is too thorough the stability of the system may be seriously affected. For this oxidation reaction Nellensteyn has given the hypothesis, that it may be compared with the formation of carbon black from gaseous hydrocarbons,[18] in this case by incomplete oxidation of mono C atomic radicals, which conforms to the following scheme.

$$\begin{matrix} CH \\ CH_2 \\ CH_3 \end{matrix} + O_2 \longrightarrow C + CO + CO_2 + H_2O.$$

The reaction may be catalytically influenced by various finely divided powders, such as portland cement, limestone, etc. In practice these catalysers are used as "fillers" to increase the stability of the mixtures. When mixing asphaltic bitumen with these fillers and at a high temperature, there is danger of too intensive an oxidation. The mixing temperature must be kept between certain limits, otherwise the overheated asphaltic bitumen may be "burnt."

Iodine Reactions.

By adding iodine to solutions of asphaltic bitumen the micelle is easily destroyed.[14] The difference in this respect between iodine and the other halogens, which react much more slowly, although being more reactive in other respects, is a consequence of the capillary activity of iodine. Iodine is adsorbed by the carbon ultramicrons; in this way it enters into the inner micelle, where it may react with adsorbed protective bodies. Quantitative researches on these iodine reactions have not yet been made. They might do much to elucidate the problem of the inner structure of the asphaltic bitumen micelle.

Hydrogenation and Cracking Reactions.

Although elaborate investigations on these reactions have been made in connection with the well-known Bergius process for the hydrogenation of coal, little attention has been paid to the colloid chemical side of the problem. The formation and destruction of asphaltic bitumen micelles are stages in the Berginization process; we know very little about the way in which these processes go on, nor of the part played by the liquids which are apt to form a more or less stable coal suspension.

Natural Asphalts.

There are only few natural asphaltic bitumens, e.g. *gilsonite.* Most of these products are *asphalts,* i.e., mixtures of asphaltic bitumen and inorganic minerals. These may be limestone (Val de Travers, Limmer, Sicily), clay or volcanic ash (Trinidad).

The construction of the micelle in all these asphalts is the same. The ultramicrons consist partly of elementary carbon, partly of inorganic material. The formation of micelles in a similar way to that of asphaltic bitumen, takes place very easily. By simply mixing asphaltic bitumen with finely divided inorganic powders, these micelles are already formed, an important fact, on which is based the application of mineral "fillers" in asphalt constructions.

The Ultramicroscopic Pictures of Asphaltic Bitumen, Natural and Artificial Asphalts.[15]

There is a marked difference between the ultramicroscopic picture of asphaltic bitumen and that of natural or artificial asphalt. There is however no difference in this respect between a natural or artificial asphaltic bitumen. Gilsonite shows the same ultramicroscopic picture as artificial asphaltic bitumens. The difference, therefore, is caused by the presence of finely divided inorganic powders in the asphalts.

The picture of asphaltic bitumen solutions is not easily obtained; a powerful light-source and painstaking focussing as well as other precautions are required. The ultramicrons are very fine and not very luminous. Natural asphalts show very bright particles which are partly much coarser than the ultramicrons of asphaltic bitumen.

The best solvent for this purpose is carbon disulfide, which has about the same surface tension as asphaltic bitumen. It has not yet been shown which other properties of the solvent play a part in this question, but as a matter of fact other solvents, e.g., benzene, toluene, xylene, chloroform, etc., are decidedly inferior to carbon disulfide for ultramicroscopic researches on asphaltic bitumen. With asphalts it does not matter which of these solvents is taken. Between natural and artificial asphalts there is no difference in this respect.

It has often been suggested that in natural asphalts the inorganic compounds had a special "colloidal" character, which should be the cause of a

supposed superiority of these natural products compared with artificial asphalts, mixtures of asphaltic bitumens and fine powders. The different ultramicroscopic pictures of asphaltic bitumen and natural asphalt have been used to support this supposition. The fact, however, that an artificial asphalt shows the same ultramicroscopic image as a natural one, proves that this supposition is incorrect. There is no question of a colloidal character of all the inorganic matter in natural asphalt. Only a very small part of this inorganic matter in natural as well as artificial asphalt is really microscopically invisible. Here the ultramicroscope shows itself a useful instrument in an important technical question.

The stability conditions seem to be the same for natural and artificial asphalts. The surface tension has not yet been determined for these materials; as long as this important datum fails, no definite characterization of these systems can be given.

Allied Systems.

Among the colloidal systems which are closely related with asphaltic bitumen and asphalt, the most important are the *coal tars*. The construction of all these systems is the same; the ultramicrons of coal tar consist of elementary carbon, partly of ultramicroscopic size, partly much coarser. Protective bodies and medium differ considerably from those of asphaltic bitumen. This is expressed by the much higher surface tension of coal tar, as compared with that of asphaltic bitumen. This high surface tension favors the peptization of the carbon ultramicrons; therefore a much coarser carbon can be kept in solution.

Reversible Flocculation in Coal Tars.

The surface tension of the medium, which for coal tar is also the principal factor in flocculating and peptizing reactions, is about 8 dyne/cm. higher than for asphaltic bitumen. Consequently the critical surface tension which determines the peptizing or flocculating character of a liquid (which must be miscible with the medium of the tar), has a higher value for coal tar than for asphaltic bitumen. Liquids which are peptizing reagents for the latter may be flocculative for coal tar. As such, carbon disulfide, benzene, toluene, etc., may be mentioned. Peptizing reagents for coal tars are nitrobenzene ($\sigma_{26,6} = 42,5$), aniline ($\sigma_{26,2} = 42,5$), furfurol ($\sigma_{29,9} = 40,7$) and *o*-nitrotoluene ($\sigma_{25} = 40,9$).

In the definition of asphaltic bitumen, CS_2 has been chosen as the solvent which determines the bitumen content. For asphaltic bitumen this is correct, the surface tension of CS_2 and the latter being about the same; but for coal tar the "tar bitumen" should be determined with a solvent having the same surface tension as the tar, e.g., nitrobenzene, aniline.

In asphaltic bitumen the organic part, which is insoluble in carbon disulfide, may be really considered as foreign matter, whereas in tar the precipitate obtained with CS_2, the so-called "free carbon," includes a part which may certainly not be considered as foreign. This part of the "tar bitumen" on the contrary is the most important one. It is comparable with the benzene precipitate of asphaltic bitumen, the asphaltènes, and as such provides a measure for the binding power of the tar.

Microscopic and Ultramicroscopic Images of Tar Solutions.

When investigating tar solutions microscopically or ultramicroscopically, one should make use of a solvent of about the same surface tension as the

tar, e.g., nitrobenzene. Even in dilute solutions (0.1 per cent to 0.01 per cent) the ultramicroscopic image of tar is very clear, showing many particles in lively Brownian movement. The particles are not so luminous as those of natural asphalts or mixtures of asphaltic bitumen and inorganic powders. The image is very easily obtained, no special illumination or other measures need be taken.

Very important from a technical point of view is the microscopic image of tar solutions. From this a clear insight into the value of a tar may be obtained.

As stated above, the carbon disulfide precipitates, the "free carbon," is a measure for the binding power of a tar. It is however not only the quantity, but also the quality of this "free carbon" upon which this binding power depends. For the quality of the carbon particles, their size and rate of protection, the microscopic image may give valuable information. Therefore a 1 per cent nitrobenzene solution of the tar, after filtration, is examined microscopically and the particles counted in a hemocytometer. The number of particles varies considerably, namely from zero to 60,000,000 per mm.[8] In some tars the particles are freely moving, in others they are agglomerated. A large number of fine, freely moving particles indicates good binding power for the tar. In solutions of natural asphalts these particles of microscopical size are found only in a small number, in solutions of artificial asphalts still less. If, however, a solution of an asphaltic bitumen in carbon disulfide is mixed with a finely divided carbon, especially carbon black, the filtered solution shows a microscopic image, which resembles closely that of a tar solution in nitrobenzene.

This illustrates again the special part played by elementary carbon as a lyophobe kernel in all these systems.

Emulsions of Asphaltic Bitumen and Tar.

A serious drawback for the application of asphaltic bitumen and asphalt is that they must be heated to a rather high temperature in order to be applicable in the form of a thin liquid, which is necessary for mixing, coating and spraying processes. For cold application two methods may be chosen.

1. Dissolving in solvents, such as benzene, solvent naphtha, spirit of turpentine, generally in oily liquids of sufficiently high surface tension.
2. Emulsifying with water as medium.

The first way is chosen by the paint and varnish industries. For most applications however this method is too expensive, the volatile component being lost and in many cases it is also preferable to have an aqueous medium during the mixing process. Therefore, the emulsifying process for asphaltic bitumen and tar is a technical problem of great importance. The first patents of technical value were taken by Schade van Westrum, who prepared a tar emulsion which functioned as a dust-preventing liquid (Westrumite).[16] The emulsifying process for asphaltic bitumen is of more recent date; during recent years especially, numerous patents have been taken.

Most of the technical emulsions are of the oil-in-water type, the asphaltic bitumen- or tar particles, protected by alkali soaps of fatty acid, resins, etc., being dispersed in water. It depends upon the nature of the emulsifier which type of emulsion is formed: Ca- and Mg-salts of fatty acids cause the formation of the water-in-oil type, alkali salts the other one.

According to the Langmuir-Harkins,[17] theory, the molecules of the alkali soaps are concentrated in the interface between the two phases in such a way, that the carboxyl-alkali part is orientated toward the water phase, the hydro-

carbon part of the molecule toward the oil phase of the emulsion. Owing to the solubility in oil and the insolubility in water of the Ca- and Mg-soaps, the affinity of the Ca- or Mg-carboxyl part of the molecule for the oil phase might cause the formation of an emulsion of the inverse type. Certainly the different solubility of the Ca or Mg and the alkali soaps must be the basis for the explanation of this phenomenon, while the influence of the size of the molecules on the direction of the emulsification, as supposed by Harkins,[18] is not so distinct. There are many objections to the Langmuir-Harkins' theory (summarized by Stamm and Kraemer [19]) and the researches of Finkle, Draper and Hildebrand [20] have not given sufficient support to it. There is no generally accepted theory, which might take the place of the Langmuir-Harkins hypothesis. We only know that the stability of emulsions is dominated by various factors, as given by Limburg [21] and that the formation or breaking of an emulsion is always a very complicated phenomenon, in which generally most of these factors play a part. Until now, however, it is only exceptionally possible to evaluate each of these factors separately. The study of the bituminous emulsions did not produce important theoretical data to aid in the solution of this problem.

Emulsions of Asphaltic Bitumen and Tar of the Water-in-oil Type.

These emulsions only find a limited technical application. In the industry of paints some of these emulsions are used. At the bottom of crude oil tanks an emulsion of this type often settles, sometimes in large quantities. These emulsions must be broken to recover the oil, but they do not find a special technical application.*

Emulsions of Asphaltic Bitumen and Tar of the Oil-in-water Type.

These are by far the most important ones. Generally they contain about 50 per cent of water (30 to 70, sometimes 80 per cent), a small quantity of the emulsifying agent (about 1 per cent) and asphaltic bitumen or tar. Mostly an asphaltic bitumen of the softer grades is used with a softening point of about 40° C. (Ball & Ring Standard method), but the harder grades (softening point 40° to 60° C.) may also be emulsified. Although these asphaltic bitumens are rather hard at room temperature, the system formed is an emulsion and not a suspension. The asphaltic bitumens at lower temperatures must not be considered as solids but as very viscous liquids. The bitumen particles in accordance with this emulsoid character are mostly spherical.

As emulsifying agents various substances are used; there are alkaline and acid emulsifiers; in exceptional cases there are neutral. Among the alkaline emulsifiers, alkali, alkali silicates, organic bases, alkali soaps of fatty acids, oxy-acids and resins are to be mentioned. The alkali salts of the fatty acids and oxy-acids, obtained by oxidation with air or oxygen from the solid paraffins, have been patented as emulsifiers and are used as such on a large scale. Often the alkaline emulsifiers are used in combination with proteins. As acid emulsifiers sulfonated fatty acids and oxy-acids, and inorganic salts, e.g. $AlCl_3$ may be used.

Soaps are most extensively used; if the asphaltic bitumen contains sufficient naphthenic acids, it may be emulsified by alkali hydroxides. The emulsifying action of soaps is due to several factors. Firstly, an electric one, in connection with a negative charge of the emulsified particles; secondly, the interfacial tension water—asphaltic bitumen is decreased by soaps; thirdly it is supposed that some of the hydrolysis products of the soaps form a protective film. It seems, especially, that proteins act in this way.

* Regarding these, see paper by A. E. Dunstan in this volume. J. A.

The preparation of these emulsions is very simple. The molten bitumen or tar is mixed with a hot solution of the emulsifying agent in water. In the case of soaps, the emulsifier may be formed during the mixing process by dissolving fatty acids in asphaltic bitumen and alkali hydroxide in water. Special mixers have been constructed, for instance the well-known Hurrell mixer. A thorough mixing of both phases is necessary.

Emulsions of different stability are obtained. In good emulsions the size of the asphaltic bitumen or tar particles does not vary very much, commonly from 1 to 10 μ diameter. Tar emulsions generally are not so regular. The bitumen and tar particles, especially the finer ones, show the Brownian movement.

When an emulsion stands for some time the bitumen or tar settles more or less, but by simply mixing or stirring the emulsion may generally be restored. Here a breaking of the emulsion is still out of the question. A guide for the settling velocity is Stokes' law:

$$u = \frac{2}{9} \frac{r^2 (\sigma - \sigma w)\, g}{\eta}.$$

u = settling velocity
r = radius
σ = specific gravity of the bitumen or tar
σw = specific gravity of the water phase
η = viscosity of the water phase.

Great deviations, however, may occur. The principal factor for the settling velocity, according to Stokes, is the size of the particles; coarse emulsions are apt to settle more easily than finer ones. Otherwise the settling velocity may be decreased by increasing the gravity and viscosity of the water phase. The gravity of the water phase may be increased by dissolving salts, which do not affect the stability of the emulsion and the viscosity by salts or organic substances.

Quite different from the settling phenomenon is the coagulation of an emulsion. Coagulation or breaking means that the bitumen or tar particles join together; it is a much more radical and complicated process than the settling phenomenon. As stated above there are various factors which influence the stability of an emulsion, and so there are many methods to break it. The most radical way is the chemical destruction of the emulsifier. In the case of alkali soaps this may be done by Ca or Mg salts or strong acids. For practical purposes the chemical destruction of the emulsifier is of almost no use. The practical application of these emulsions is based on the fact that mixing with various substances, such as stone, sand, paper, etc., causes a gradual breaking of the emulsion. During the breaking time the bitumen or tar must stick or adhere to the foreign matter. In order to adhere well, breaking should take place or at least start on the surface of the foreign matter. Introducing this foreign matter into the emulsion may affect the system in various ways:

1. By adsorption of the emulsifier,
2. By changes in the electrical charges and in the interfacial tension.

The result of all these changes is that a part of the water together with the emulsifier is separated from the bitumen which thus coagulates and expels the water from the surface of the foreign matter, sticking to it and binding it together. The details of all these processes are almost absolutely unknown, and it is certainly very mysterious that the coagulated bitumen easily expels

the water, while molten bitumen adheres very poorly to moistened surfaces of mineral matter.[22]

Technical Applications.

The emulsions of asphaltic bitumen and tar are used chiefly in two branches of industry, i.e. for road construction and in the roofing paper industry.

Road emulsions are prepared in different qualities, especially regarding the stability and the breaking time. It depends upon the kind of road construction which road emulsion should be applied. If the road is constructed in the same way as a cement concrete by mixing broken stone and sand with a binding material, i.e., the bituminous emulsion, a stable emulsion and a long breaking time is required. Otherwise the material would stick together too soon and spreading on the road would be very difficult.

Another construction method is *grouting* or *penetration*. In this case a road is treated with a bituminous emulsion filling the interstices between the stones. Because of its low viscosity the emulsion penetrates easily into all the cavities and also into the finer pores. For this method a rather rapidly coagulating emulsion is required in order to prevent the unbroken emulsion from seeping into the foundation.

Less stable grouting emulsions also may be used for the mixing process, but then the stones should be precoated with an alkaline solution, e.g. sodium carbonate, by which the coagulating action of the stones is decreased.

The least stable road emulsions are required for *surface dressing*. In this process the surface of a bituminous road is treated with an emulsion. Because a bitumen-coated stone has almost no coagulating action, in this case a very unstable emulsion is required.

In the roofing paper industry emulsions containing a certain amount of finely divided clay are principally used.

The industry of bituminous emulsions is growing rapidly: this "cold asphalt" indeed has many advantages in comparison with the hot mix processes. No heating or drying of the bitumen and the other materials, nor any complicated machinery are required. The quality of the products, especially in road constructions, is not as good as that of the hot mix products. But, nevertheless, there are emulsion-bound roads which stand a fairly heavy traffic. The emulsion industry is a young one and it may be expected that a considerable expansion of this promising industry will take place in the near future.

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EDITOR'S NOTE.

Mention must here be made of emulsions of tar, asphalt, and the like, prepared by using clay. German Patent No. 216,212, issued Nov. 6, 1909, and U. S. Patent 1,049,916, issued Jan. 7, 1913, to Dr. Friedrich Raschig of Ludwigshafen am Rhein, disclose emulsions of this type, and give as a typical example "stirring 200 kilos of unctuous China clay (fetter Lehm oder Ton) with about 100 kilos of water in a suitable mixing machine, and then gradually adding about 500 kilos of tar and 200 kilos of water, while constantly stirring, until the tar has been uniformly distributed." Raschig says it is useful as a waterproof paint and will adhere to wet surfaces, and can also be used in making roads. "The paint or coating has the property characteristic of clay-tar emulsions, that after drying, it is no longer absorbed by water. The paint is therefore perfectly weatherproof and owing to the presence of the clay, it possesses the following valuable properties. Unlike ordinary tar coatings, it will not soften at high temperature, and consequently not flow off, while tarred roofing gradually loses the major part of its tar-coating, when exposed to the heat of the sun. Moreover, the tar-clay paint is far less combustible, and woodwork or roofing coated with it will therefore propagate fire very slowly." The claim covers "a protective paint consisting of an emulsion of tar, clay and water," with a second claim for the process of making the emulsion by stirring tar and water into a mixture of clay and water.

A further advance was made by Clifford Richardson, who found that clays high in colloidal content were especially suited to making clay-asphalt emulsions, the manufacture of which he describes in U. S. Patents 1,198,769 and 1,198,955 (both Sept. 19, 1916). He employs "a fine clay having within it a sufficient proportion of matter capable of colloidal dispersion in relation to water, as can be ascertainable by proper examination. Ordinarily, the disperse colloid is associated with a larger amount of fine material not in such colloidal state." The excess of non-colloidal matter may be removed, e.g., by elutriation, and other colloidal materials than clay may be used. The amount of colloidal material should be at least one or two per cent, but may be more. "The amount of colloidal material must not, however, be so great as to prevent the bitumen from constituting a continuous phase in relation to the clay dispersed therethrough," after elimination of the water originally used to make a paste of the clay. "Proper agitation of the paste and the bitumen with steam or air will effect an emulsion of the two components." As an example, Richardson mixes with a bitumen liquid below the boiling point of water, from 20 to 50 per cent of a liquid paste containing disperse colloidal matter, varying in amount according to the quality of the clay, but, of course, the more desirable the larger percentage of this material, although the coarser portion may be looked upon as desirable as an ordinary filler.

Richardson's claims were directed towards the final product, left after the emulsion dried out, the emulsion itself being an intermediate but essential step in the procedure. He was quite familiar with bentonite, for the writer had sent him some; but he was able to make out with a local clay, just as Raschig had done. Raschig's clay, however, was very low in colloid content. The subsequent issuance of patents for making emulsions of bitumenous substances with the aid of aqueous dispersions of colloidal clays, and especially bentonite, is perhaps due to the fact that Richardson's disclosure of such emulsions was probably filed under the general class of "Plastic Compositions," sub-class "Bituminous and Resinous," indented under "Artificial Stone"; and consequently it would not meet the eye of an examiner looking over the class, "Liquid Coating Compositions," where most "emulsion" patents go.

When the clay-water-bitumen emulsion dries out, the residuum has a much higher melting point than the bitumen used, because of the finely divided clay in it. The writer long had two tubes prepared by Richardson containing spirals of the same asphalt, to one of which the same amount of the same colloidal clay had been added dry, while to the other the clay had been added as a wet slurry as per Richardson's patents. The former slowly "ran" in warm weather, while the latter never lost shape.

L. Kirschbraun has taken out numerous patents covering specific uses of clay-asphalt emulsions, to which, e.g., he adds paper pulp in the beater, and flocculates with alum, sodium silicate, etc., to get a waterproof paper. See U. S. Patents 1,302,810, 1,461,445, 1,506,371, and 1,567,061.

Deflocculated Graphite *

By Edward Goodrich Acheson.

In 1901, the author, in an attempt to utilize his electric furnace graphite for crucible production, sought to employ domestic clays as a binding material. Many difficulties were encountered, however, and not a little confusion resulted in endeavoring to find whether the fault lay with the graphite or with the clay.

At that time the crucible makers of the United States were using clays imported from Europe—particularly Germany—as they showed marked superiority over domestic clays both in plasticity and tensile strength. An analysis of the European and domestic materials failed to reveal any unusual differences in their chemical composition to account for their dissimilar physical properties.

It has been common knowledge among clay workers, however, that residual clays were usually of low plasticity, while sedimentary clays were inclined to be highly plastic. This afforded a starting point in the solution of the plasticity problem.

Plasticity occurring in sedimentary clays and not in residual, seemed to have been developed by, or during, the transfer from their place of origin to their final beds. The water effecting the transfer acquires, usually, in its passage through fertile regions, considerable organic matter of vegetable origin. This fact suggested the initial methods to be pursued in an attempt to duplicate Nature's method of imparting plasticity.

Although the very early attempts to solve this problem resulted negatively, encouraging effects were soon noticed when gallo-tannic acid was substituted for the simple organic compounds previously employed. Tannin not only gave the desired fluidity with less water but produced upon further examination, an increase in tensile strength and plasticity. It was also noted that the clay particles after such treatment remained diffused in water and were so fine as to pass through the pores of filter paper.

A search of the literature to find in the history of clay-working some record of the addition of organic matter for the improvement of plasticity was fruitless, except for the single mention of the use of straw in brick-making by the Egyptians, as related in the fifth chapter of Exodus.

Feeling the use of straw as a mechanical bond was not nearly as valuable as many other vegetable fibers of greater strength available to the Egyptians, the author believed its use must have been for some other reason. Carrying out this theory, an extract of oat straw in water was used in place of tannin and produced results equal to the best previously obtained. It is interesting to note that a certain clay so treated, showed greater tensile strength in a

* When Dr. Acheson exhibited his deflocculated graphite at a meeting held in the old building of the Chemists' Club in West 55th St., N. Y. City, Oct. 17th, 1907, the Editor, who was translating Prof. R. Zsigmondy's "Zur Erkenntniss der Kolloide," recognized it as colloidal graphite, and soon thereafter exhibited in the ultramicroscope a sample which Dr. Acheson kindly gave him at the time. Later, he exhibited it to Dr. Acheson and made estimates of the size of the particles, which Dr. Acheson referred to in an address given on Nov. 6th, 1911, before the London Section of the Society of Chemical Industry. (See *J. Soc. Chem. Ind.*, **30**, 1426-9 (1911). J. A.

briquette dried at 100° C. than a burnt brick of similar clay untreated and untempered. It was, therefore, possible for the Egyptians to produce a sun-dried brick of greater strength from straw-treated clay than from the same clay untreated and unburnt.

Believing the Egyptians were familiar with, and practiced this art, the author thought it appropriate to recognize that fact by calling the treatment "Egyptianizing" and the product "Egyptianized Clay."

Having succeeded in manufacturing a graphite eminently suitable for lubrication purposes, the author desired to make it available for that application. Its incorporation in grease presented no difficulties, but when efforts were made to diffuse it in oil, the graphite settled out rapidly.

Remembering the diffusing effect of tannin upon clay, the author, in 1906, investigated the effects of tannin upon graphite, utilizing the method developed in producing Egyptianized Clay. The results were very satisfactory, producing a graphite of such reduced particle size as to remain indefinitely diffused in water. Further experiments resulted in the successful transference of the graphite from its aqueous carrier to an oil medium, thus making it possible to employ Acheson Graphite in oil as well as in grease.

In a paper, "Egyptianized Clay," which the author wrote for private distribution in 1904, were recorded his experiments on the colloidalization of clay. Being unfamiliar with the ceramic field, the author retained Heinrich Reis to test the clays he treated so as to prove the truth of the author's discovery. Dr. Reis fully corroborated his findings.

The term "deflocculation" suggested itself as describing the breaking down of the compound grains to those of colloidal dimensions. The author continued to use this term for describing the same process on any material.

Deflocculation is possible not only with tannin and extracts of straw, but with numerous other organic materials, including sumac, oak-bark, spruce bark, tea leaves and dextrin. The deflocculation effect also is not limited to graphite but may be successfully applied to a vast number of substances among which are silica, alumina, siloxicon, lamp-black, sulfur and lead arsenate.

Deflocculation, therefore, takes its place among the methods to be utilized in the colloidalization processes of practice as well as theory.

The Deflocculation Process.

By deflocculation, the author means a process of chemico-physical disaggregation of coarse particles, into particles of colloidal dimensions. The writer conceived all solid material to be built up of multimolecules having colloidal dimensions and held together by surface forces. He considered a coarse particle of matter to be porous, having submicrocapillaries throughout.

In all hydrophobes it is found that the surface tension of water is greatly reduced. A lowered surface tension, therefore, is a required condition. Tannin dissolved in water considerably lowers the surface tension and concentrates at the interface. If an aqueous solution of tannin is permitted to stand in a beaker, a hard crust of tannin will be found on top of the solution, at the interface liquid-air. When, to such a solution, a substance such as powdered clay be added, a realignment of the internal forces results. If another interface is introduced, the tannin will then concentrate itself at the interface water-clay. The clay is found to adsorb the tannin. Due to internal capillary forces of the clay particles, the tannin solution will travel through the capillaries, and, to equalize the surface forces, surround the multimolecules or

aggregates of colloidal size with tannin solution. Tannin will concentrate around the small particles due to concentration at the interface clay-water, forming a coating of tannin, probably mononolecular in thickness. All the particles become charged alike and are forced apart.

A typical laboratory experiment illustrating the procedure followed in deflocculating solids, follows (see Fig. 1):

To 750 grams of graphite is added 37.5 grams of tannin dissolved in 236 grams of water. The mixture is stirred for five minutes, after which time a sample of the resulting paste is taken and agitated in sufficient water to disperse the deflocculated fraction and permit the non-deflocculated portion to settle out. The tube containing the deflocculated portion is set aside for comparison with similar samples taken while the mixture is continually subjected to stirring at time intervals of 15 minutes, 30 minutes, 45 minutes, one hour, two hours, four hours and five and one-half hours.

After the dispersion, samples are permitted to stand 24 hours, a drop from each sample tube is permitted to fall upon filter paper, and allowed to diffuse. The resulting test spots (*see* illustration) indicate the progress of deflocculation.

It will be observed that Spot No. 1 (after 5 minutes) shows a small degree of dispersion, which increases with time as may be noted by reference to the subsequent spots.

The degree of dispersion is dependent upon several variables; i.e., percentage of deflocculating agent, time, moisture, temperature, etc. Spot No. 8 very well illustrates the effect of added moisture.

Spots 1, 2, and 3 were observed to have a pronounced external ring, brown in color due to unadsorbed tannin. The color of this ring became lighter in successive tests, ultimately disappearing, indicating increased adsorption to the graphite with a consequent increase in deflocculation.

It is apparent, from a study of deflocculation curve, that when the moisture is kept within the indicated limits, deflocculation increases with rise of moisture within those limits. From the viewpoint of adsorption, graphite will adsorb the colloid from solution when the water concentration is kept between these limits, but beyond these limits adsorption falls rapidly, and consequently the degree of deflocculation falls as a direct function.

It was observed that a rest period during the process of deflocculation has beneficial results in that it increases the efficiency of the procedure. It was the author's opinion in his original experiments that a period of rest would permit of a period of adsorption of the deflocculants by the graphite. The mass was again subjected to movements followed by another period of rest. This procedure was followed repeatedly.

Bancroft, in his "Applied Colloid Chemistry" (1921), p. 266, mentions a rest period in the formation of emulsions when making mayonnaise. There is apparently some physical change which takes place during this period of rest.

There is a distinction between deflocculation and peptization. Graham used the term peptization to describe the liquefaction of a gel. Usually only small traces of an agent are required to peptize any given material, as for instance the peptizing of clay by sodium hydroxide. Usually only 0.5 per cent of the base is required. To be peptized, most materials require a specific agent. Alkalis will peptize clay, but will not peptize, for instance, chrome yellow. Deflocculation, on the other hand, is more general in its application. A common agent will deflocculate clay as well as chrome yellow. In deflocculation, mechanical action is required, while in peptization no mechanical action is necessary.*

* The kinetic activity of a peptizer is a potent factor, as may be seen by following ultramicroscopically the action of diastase and pepsin [see J. Alexander, *J. Am. Chem. Soc.*, **32**, 680-7 (1910)]. *Time* is also an important factor; and even pepsin, from whose action Thomas Graham framed the word "peptization," takes time to act. Time is also important in the weathering of rocks and in the ageing of clays, for ceramic uses, though here, as in other delayed actions, microorganisms and chemical changes may supervene.

Etymologically, "deflocculation" involves reversing the formation of flocks (or flocs). The par-

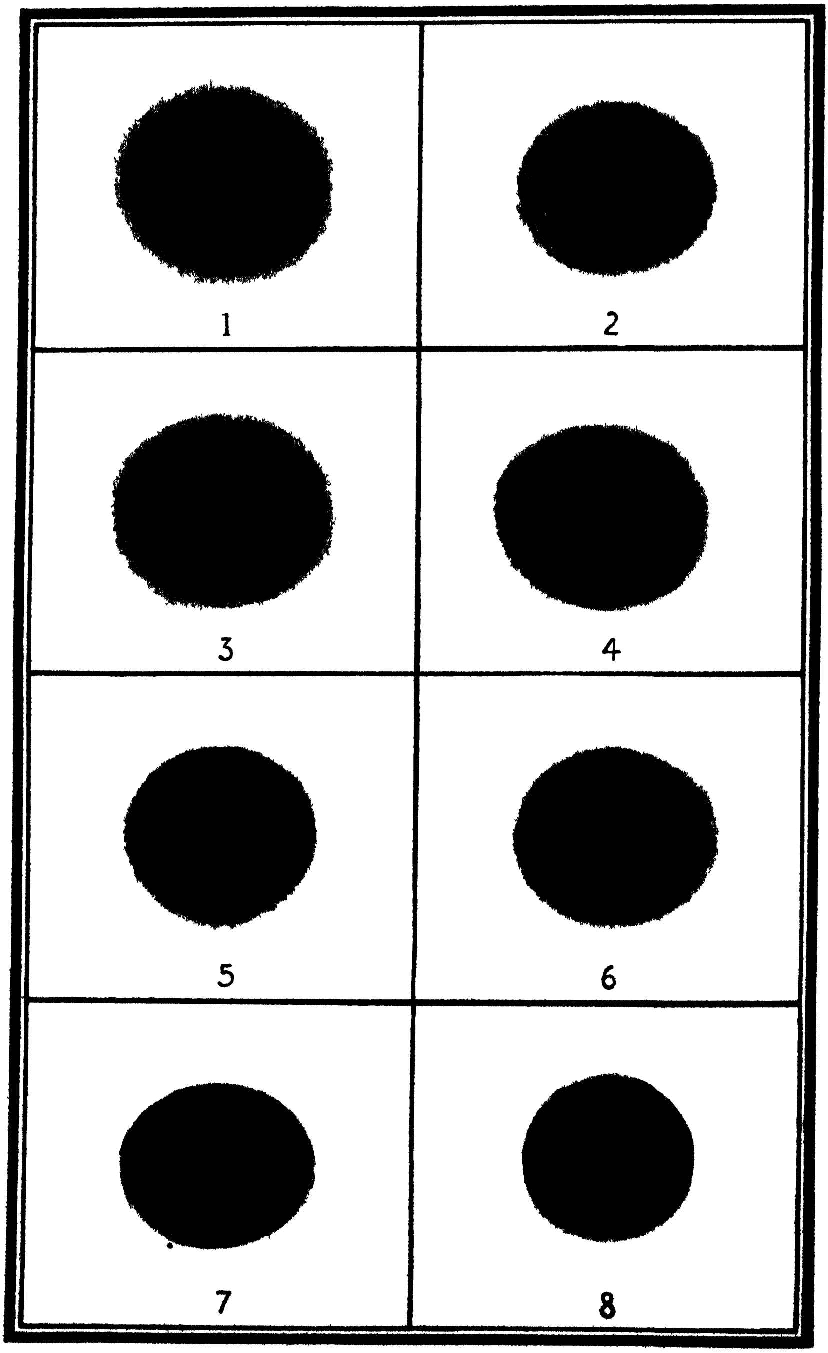

Fig. 1.

To illustrate the latter point, Prussian blue stirred into water may be dispersed by either peptization or deflocculation. The addition of 0.5 per cent oxalic acid solution to the Prussian blue will immediately disperse same. Tannin also will bring about the dispersion of Prussian blue, but not without the aid of mechanical action. It should be kept in mind, however, that mechanical action does not infer grinding.

Kruyt ("Colloids," New York, John Wiley & Sons, Inc, **1927**, p. 156) states "In case no mechanical subdivision takes place, and yet the method of preparation is one of dispersion, the inference is that primary particles of colloidal dimensions were originally present."

Kruyt further states that a substance may be ground to the limits of 1 μ where it is suitable for the sol formation. Where no grinding takes place, the method of preparation is one of dispersion. He infers that primary particles are present, followed by peptization. This latter view coincides with the author's, as described above; that is, in the construction of the particles. The author goes farther in that he believes *all* particles are composed of primary particles held together by surface forces. An increase in the boundary potential by means of a peptizer carries the primary particles to the colloidal condition.

Von Weimarn in his "Theory of the Colloid State of Matter" states: "I have no knowledge that, up to 1906, any of the investigators of colloids had ever set himself the task to disclose—by way of a systematic experimental investigation of the process of crystallization of different substances from solution—the transition conditions from colloid to crystalloid and vice versa, which conditions remained a mystery to Thomas Graham."

The writer, in 1905, observed the transition of noncolloidal matter to the colloidal state by a process of deflocculation. The author had studied the phenomena systematically, resulting in a method to reduce many crystalloidal substances to a colloid state. (Ref. *J. Franklin Inst.*, Nov., 1907.)

To quote von Weimarn again: "For a given substance, no sharp boundary lines may be drawn between the colloids, the amorphous and the crystalline states, since the mutual transition from one state to another is affected by degrees." This was aptly demonstrated in the author's laboratory. For example: dry crystals of lead chromate were deflocculated and were then shaken up in a large quantity of water and elutriated. It was possible to collect colloidal crystals as well as very coarse ones, and the transition between both was very gradual—practically indiscernible.

The author, in his presentation before the American Electrochemical Society in 1907, described and demonstrated the deflocculation of graphite and had expressed the belief based upon experiments and observations that graphite, for instance, could be so treated as to be able to obtain particles from the very coarse to molecular, going from stage to stage, with a very uniform increase in specific surface, and no sharp break was observed.

The above observations are founded upon a large series of experiments. A mass of powdered graphite, for example, may be deflocculated and the dispersed portion floated away. The tailings remaining after the initial deflocculation may then be simply treated and another yield of deflocculated

ticles forming the flocks, as in the case of clays and chemical precipitates, need not necessarily be of colloidal dimensions. Deflocculation, therefore, does not essentially involve reduction to colloidal dimensions. On the other hand, "peptization," as a rule, connotes a rather profound subdivision, which may be accompanied by chemical change and may lead to molecular dispersion. Basically the two processes are alike in that in both some new phase, usually liquid, insinuates itself between the constituent particles of a substance, the attraction of the particles for this new phase being stronger than their attraction for each other. Just how profoundly this breaking-down process proceeds will vary with the dispersing agent, the substance dispersed, and the conditions of the experiment. J. A.

material obtained. The tailings remaining from each successive treatment may be deflocculated until the entire mass has been dispersed. It should be kept in mind that no grinding action was resorted to.

Practical Applications of Deflocculation.

The possible industrial applications of deflocculation are too numerous to discuss in this brief paper. A few examples, however, will suffice to illustrate the growing importance of this process.

In the production of paints and varnishes it is generally agreed that the fineness of the pigment is an essential factor in a good product. The fineness of pigment size not only contributes to the covering power of a paint, but controls opacity and oil adsorption as well. Deflocculation will produce the pigments in colloidal condition in oil and also control the particle size.

The ceramic industries offer a fertile field for colloid research. Considerable work has already been done on the colloidal properties of clay. In the author's laboratory a doll's head was made, using a hard porcelain mixture of deflocculated flint, feldspar and china clay. The head was cast in a plaster mold, dried and fired at cone 12 for fifteen minutes. After cooling, the surface was found to have an exceptionally smooth waxy appearance as if glazed.

Another field of application is in the fabrication of rubber goods. In 1923, in the author's laboratory, deflocculated pigments and fillers were blended with rubber latex upon coagulating (or reflocculating) the mixture. A very homogeneous mass resulted. It is well known by workers in the industry that long milling reduces the tensile strength of rubber. By the deflocculation method, the milling is reduced to a minimum, resulting in a superior product.

The deflocculation process applied to graphite, serving to produce the brands of graphite hydrosol and oleosol sold under the trade-marks "Aquadag" and "Oildag," is probably the best known industrial utilization of the method.

The laboratory experiment described above is given commercial significance when performed on a large scale with specially devised equipment, one of the commercial units processing ten tons of graphite at one time.

"Aquadag" is a graphite hydrophobe, while "Oildag," as the name implies, is an oleophobe. The lubricating quality of colloidal graphite is due to its adsorption by bearing surfaces forming a protective film against wear. The colloidal graphite permits the lowering of interfacial surface tensions between lubricating oils and metals. It may readily be shown that lubricating oil containing colloidal graphite will spread over a surface with greater ease and remain on the surface, keeping it permanently wetted.

The best-known method for the measurement of yield of lubrication is the heat of adsorption—the higher the heat of adsorption, the greater the lubricating value. Oil containing colloidal graphite has a higher heat of adsorption than oil without colloidal graphite. Less oil, therefore, is necessary for efficient lubrication. A clean piece of metal immersed in "Oildag" lubricant, without any mechanical action, will adsorb a film of graphite on its surface, which is impossible to remove unless by abrasion.

Graphite hydrosol ("Aquadag") has very unique properties, which are interesting from a practical point of view as well as the theoretical. Its physical properties are such that it may be applied in many of the arts. Because of its colloidal nature it permits of the formation by the adsorption upon surfaces where it is desirable to conduct a current of electricity. Some applications of this are in electrotyping, grid-leak manufacture, volume con-

trol production. It is also used for impregnating cloth, paper and other materials. An interesting application is metallizing glass, where the glass is given a film of graphite adsorbed from the hydrosol and then plated in the usual manner in the electrolytic bath. Its lubricating qualities lend themselves readily to the drawing of wire such as tungsten and molybdenum and in steam cylinders and compressors. Its inert qualities permit its use as a parting compound in rubber molds, for example, and die casting. Its opaque qualities make it valuable in photography where it is used for the purpose of shading. Its many desirable qualities in that it is inert, opaque, indigestible and harmless biologically, have been recognized as useful in physiological experimentation. It has recently been used for the purpose of lining intestines of living animals for X-ray work. It is being used in boiler feed water to effect reduction in scale formation.

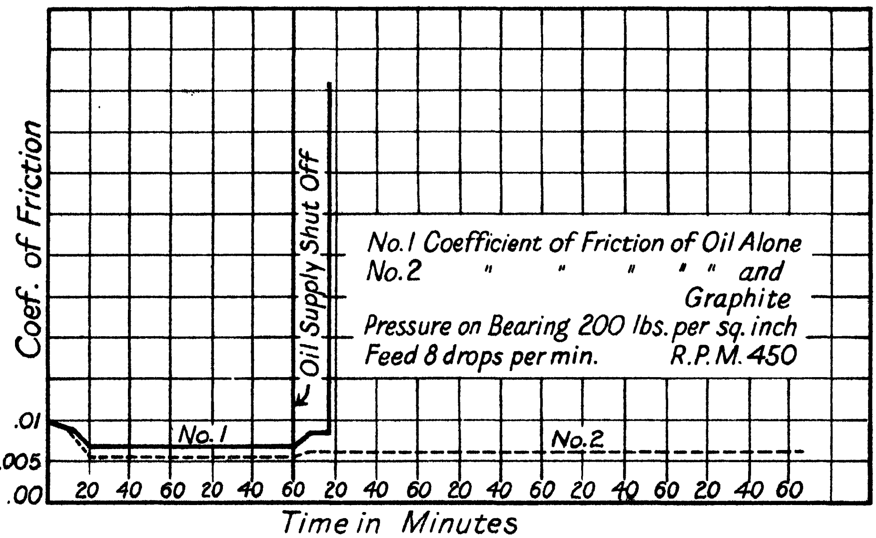

Fig. 2.

The adsorption properties of deflocculated graphite are demonstrated by a simple experiment. Allow a polished strip of steel to remain for several days half immersed in oil containing colloidal graphite. Remove the steel and wash free from any adhering oil. The author washed the steel with xylol and ether. The part of the steel which has been submerged will have a film of adsorbed graphite. It will be found very difficult to remove this film except by burning or severe abrasion. The metal surface having the adsorbed graphite has its residual valence satisfied. The saturation of this valence decreases the interfacial tension between metal and oil. This may be observed by placing a drop of oil at the line of division so that half of the drop will be on the steel while the remainder is in contact with the "graphoid" surface. It will be found that that part of the oil drop over the "graphoid" surface will spread itself rapidly into a thin film, whereas the drop over the steel will spread much more slowly. This was due in a measure to the rapid spreading on the "graphoid" surface which depleted the drop.

This simple experiment with the strip of steel demonstrates exactly what

occurs on metal surfaces on bearings and other surfaces subjected to friction where the lubricating oil contains colloidal graphite.

A direct result of the decrease in surface tension is measurable by determination of the coefficient of friction. Dr. Mabery investigated this and found a decided lowering in the coefficient of friction when colloidal graphite in oil was used.

Dr. Mabery's results were confirmed by tests carried out at the National Physical Laboratory (England) in 1928. The laboratory tests determined the influence of colloidal graphite in lubricating oils and were made on white metal bearings lubricated with a minimum quantity of oil and oil containing colloidal graphite. "It was found that a bearing lubricated with mineral oil to which Oildag had been added would run with about one-third the minimum lubricant required with the same mineral oil without Oildag." It was also found that the feed of oil could be reduced appreciably, as much as 60 per cent. The National Physical Laboratory report continues: "This may be caused by the formation of a 'graphoid' surface on the journal and bush so that less oil will produce a film of sufficient thickness to carry the loads, or it may be caused by improved lubricating qualities due to the presence of graphite."

It is the author's opinion that both factors—reducing surface tension and graphoid surface—play their respective parts in the lowering of the coefficient of friction.

Any colloid in the oil will reduce the surface tension, enabling the oil to spread completely over a surface, but graphite is the only available substance which is not only an efficient lubricant but is extremely stable, due to its elemental character, thus making it capable of withstanding high temperatures and pressures. Many attempts have been made to add colloids to oil so as to lower the surface tension. Amongst other substances used are the fatty acid salts of the heavy metals which dissolve in a colloidal condition in oil. These salts break down readily under the influence of high temperatures and pressures with consequent loss of efficiency as a lubricant.

Wells and Southecombe [*J. Soc. Chem. Ind.* (1920), or *Chem. News*, **120**, 244 (1920)] found that by adding a small amount of fatty acid to a mineral oil a much-improved lubricant was obtained. Archbutt and Phillip [*Chem. News*, **120**, 269-70 (1920)] in a discussion on the "Germ Process" endeavor to explain the action of a fatty acid in terms of adsorption. Archbutt suggested that Deely in a communication to the Physical Society, expressed the probable effect when he said that the unsaturated molecules of the lubricant united with the solid metal surface and formed a new surface which offered less resistance to shear than the unlubricated metal surface. Phillip expressed the belief that metallic soaps were formed by the action of the fatty acids on the metal bearings.

Like any other lyophobic colloid, graphite in the colloidal state does not increase the viscosity of the medium in which it is suspended.*

CONCLUSIONS.

It is evident from the remarks contained in this brief paper that the subject of deflocculation affords a fertile field for research and it is the author's belief that properly directed endeavor will result in extensive applications of this method to many of the arts.

* This, of course, applies only to relatively dilute dispersions. J. A.

Colloidal Fuel

By Lindon W. Bates *

As originator of the term, I have defined "Colloidal Fuel" for the Century Dictionary as follows:—"A stable mobile atomizable fuel displaying colloidal characteristics, comprising particles of solids, droplets of liquids or minute bubbles of gases, or combinations thereof, suspended in one or more varieties of liquid hydrocarbons." Just as the briquette is the composite solid fuel, so colloidal fuel is the composite liquid or liquefiable fuel, whose colloidal or colloid-like components remain intermingled but wholly or partially in separate phases. Heretofore, there have existed solid, liquid or gaseous combustibles, but the art of successfully permuting these distinct kinds of fuels in a liquid base had been barely conceived in earlier experience. Past knowledge was crystallized, and the science of such composites was carried into far broader realms by the research conducted under my direction and guidance during the war years. Colloidal chemistry was carried into the fuel industry and, in fact, a new branch of chemistry—that of stable coarse suspensions—has been unfolded as a direct outgrowth and extension of the colloidal.

In view of the well-known economic and operative advantages of atomizable over solid fuel, the occurrence of solid carbons unsuitable for commercial use in their encountered form and the high value and comparative scarcity in many lands of certain oils, there has long been felt the desirability of evolving a process for combining the cheaper or more plentiful sources of solid carbon with liquid hydrocarbons in such a fashion as to admit of spraying and the simultaneous combustion of the components. The more available carbons are generally solids, such as coals and cokes. Attempts have been made in the past to make a liquid fuel of fine coal and oil and of coal tar with oil, but as petroleum is not a solvent of coal or tar, comparatively rapid and uncontrolled separation, settling out or sedimentation of some of the components has, heretofore, discouraged the industrial use of such mixtures. In colloidal fuel the sciences of chemistry and physics have at last been made to disclose satisfactory ways to produce the desired composite. Even more has been done, as a whole new range of sprayable fuels has been created.†

For a fuel to be atomizable and for its components to be simultaneously combustible, it is necessary that the fuel be mobile, and that it enjoy adequate stability for storage and for use in a given temperature-range, and for enabling it to pass through the pipes, preheater and other apparatus parts, without clogging. The degree and duration of the adequate stability desired vary according to the contemplated handling and use of the fuel. For marine and industrial uses, the character may be coarser than for internal combustion engines. For some purposes a few minutes of stability are alone required. This is the case when the fuel is burned directly after preparation. For other purposes, as when storage is intended, stability not merely for some days, but even for months may be desired. To give the utility character required, it is essential to prevent or delay the settling to the bottom of the medium or

* Mr. Bates died in Paris shortly after completing this paper. The experimental and chemical work was carried out at the Eastman Kodak Laboratory under Dr. S. E. Sheppard. J. A.

† In recent years there has been an extensive development in the use of dry powdered coal, etc., the powdering being done just prior to combustion, as a rule. J. A.

floating to the top of the minute portions of dispersed substance for a reasonable length of time and to a reasonable extent, depending in duration and degree upon several variable factors. These include the length of proposed storage after manufacture, and the type of combustion, conveying and spraying systems. While an unstabilized composite is of doubtful utility, save under very exceptional circumstances, prolonged stability is not necessary for the practical utilization of the fuel. Occasional movement in storage or after prolonged standing to promote a new cycle is not a hardship. Stability for a month or two is ample for nearly all purposes.

The problem, theretofore, has been to bring equality or approximate equality to the two sides of Stokes' well known equation, modified to allow for the non-coincidence of the factors in hand with the theoretical factors upon which Stokes' Law is predicated. In order to achieve adequate or relative stability of the particles in the medium so as to permit continuous spraying without the need of constant agitation, an equilibrium of the various forces in the composite was necessary. The velocity of the ascent or descent of the particles, droplets or minute bubbles had to be brought to zero or nearly thereto for the viscosity range of the medium corresponding to the temperatures of storage and best preheat. Internal conditions had to be established or modified whose combined results would be to neutralize temporarily or permanently the effect of gravity.

A number of distinct or distinguishable methods of achieving stability have been evolved. Three only of these—not necessarily the preferred methods—will be now listed: First it is possible to stabilize particles by the use of certain protective substances. Soap solutions may be mentioned. Some of these are operative not only upon colloidal coal in oil but also upon particles in size far above colloidal dimensions. Of the fixateurs, a typical substance is a variety of lime-rosin grease, specially prepared, in which lime, rosin and water are incorporated with heat and circulation into an oil carrier. Second, it is possible to peptize bituminous coals and some other solid carbonaceous substances, to a limited but sufficient extent for stabilizing purposes, by the addition of percentages of coal distillates, such as tars and the middle fractions, and by subjecting the mixture to a special heat treatment below the flash-point temperature. Third, by intensive grinding, it is possible to reduce coal to colloid size, or practically so, and thereby to achieve the stability inherent in smallness of dimension. These and other measures are readily combined so as to adapt the stabilizing treatment to the specific gravities, surface tensions, viscosities and association tendencies of the several ingredients. It is entirely possible to stabilize in mineral oil in readily liquefiable form up to 55 per cent of foreign substances divided between the liquid and solid ingredients derived from coal. A very suitable fuel consists for example of 30 per cent coal, 10 per cent coal tar distillate and 60 per cent fixated mineral oil.

The percentage of particles which may settle out during the life of the composite, depends upon the treatment given. The first colloidal fuel made for U. S. S. Gem carrying 31 per cent Pocahontas coal in fixated navy fuel oil, was used and tested on that vessel for more than five months with the assistance among others of Haylett O'Neill. At the close of three months, the small settlings were stirred into oil, thereby renewing its "life." Since those early days the fuel has been materially perfected. Thus, with regard to Grade 15 carrying 38 per cent mixed coal and coke stabilized in fixated Mexican oil, after special tests merely 2.6 per cent of the particles had become destabilized in five months, and that the fuel displayed various colloidal characteristics, such as Brownian movement. Grade 16 of the fuel with 42 per cent mixed

coal and coke stabilized in fixated Mexican oil, was successfully burned eight months after manufacture, during which time the barrels had been exposed in the open air to frost and weather without any motion treatment other than that necessarily involved in coil heating and removing the material from the barrels.

The colloidalizing process has broadened out in many important directions. Thus the combination therewith of the froth-flotation system for the separation of ash from coal has been investigated. The effect of coal storage and water seals in regard to decrease of fire hazard has been tested. The adaptation of a low-ash composite to Diesel engines has received special attention and the preparation for this purpose of a true colloid of carbon in oil is considered to have already been achieved and is being further developed.

In regard to the physical characteristics of the fuel the Underwriters Laboratories of the United States National Board of Fire Underwriters undertook a series of elaborate tests extending over six months. Certain salient sentences in their final Report of March 24, 1920, adopted by the inner Fire Council of experts, deserve quotation and confirm the claims made for the fuel: "The material is practicable for use as a fuel for ordinary burning purposes, and presents no objectionable characteristics for such purposes when compared with ordinary fuel oil." "It is not affected by sea water, and will probably not be affected by any chemical action arising from contact with a steel or iron tank or container." "Tests with salt water produced no apparent effects, nor did high temperatures show any visible change in the physical state." "Colloidal Fuel is practically non-volatile. Its flash-point is very much higher than is usually found in fuel oils." "The apparent ignition temperature is likewise relatively high. The material shows no tendency towards spontaneous ignition." "The fire hazard of the product in storage and use is moderate, and is judged to be less than that of ordinary fuel oil, having a flash-point of about 150° to 180° F."

From the economic point of view colloidal fuel possesses many advantages over fuel oil or coal alone. First, the fire hazard of colloidal fuel is less than that of oil or coal. The specific gravity of a composite using over about 15 per cent of coal is greater than unity. If on fire, the flames may be quenched in and by water, and, in storage, fire may be prevented by a water seal. This fact is of cardinal importance as other liquid fuels are lighter than water and cannot be so safeguarded. Trials of a water seal have shown that certain grades of the fuel may be so stored for even a year without jeopardizing their operative character. Sprinkler systems of fire protection do not lose their utility as they do in plants using oil fuel. The insurance advantage and increased safety of ships and plants due to this fireproofing capacity is obvious. It has been found also by experience that the addition of carbonaceous particles to an oil and the proper association of these components, tends to materially raise the flash-point of the oil and reduce evaporation. It may be that the volatiles of the oil have a preferential affinity for those of the coal or are preferentially absorbed by, and adsorbed with, the particles. In any event, colloidalizing imprisons an important part of the volatiles of both. The Report of the Underwriters' Laboratory emphasizes this interesting phenomenon. The flash-points of most colloidal fuels vary between 250° and 280° F. There is, therefore, far less risk in the handling and utilization of colloidal fuel than with fuel oil, and it is no longer necessary, as is the case with many oils, to preheat close to or over the flash-point, to reach the best atomizing range. For these several reasons the Fire Council in the United States gave a colloidal fuel a preferred rating over fuel oil, and the new liquid combustible was ad-

mitted by the Board of Standards and Fire Chief more willingly than oil for combustion use in the City of New York.

Second, the good grades of colloidal fuel possess more B.t.u. per volume than either of its principal components separately. This is due to greater specific gravity. The addition of coal or tar is by no means an adulteration of oil. It may be an enrichment. For example, using 65 per cent oil, of 18,500 B.t.u. per pound (which is 177.600 B.t.u. per imperial gallon) and gravity 0.96 with 35 per cent bituminous coal of 14,000 B.t.u. per pound and 1.4 gravity, the resulting colloidal fuel is heavier than water and has 182,800 B.t.u. per imperial gallon. A special grade of Navy fuel using crude oil coke of 15,000 B.t.u. and density of 1.8 will have 198,000 B.t.u. per imperial gallon or 12 per cent more than the oil. This means that where storage space is of importance and weight is of lesser moment, greater heating capacity and steaming radius may be obtained by using the composite than by using oil alone and much greater than by using coal.

Third, colloidal fuel may be prepared having greater combustion efficiency than straight oil. This is true of peptized mixtures and may be explainable by the probability that the liquid film on the outside of the particle gasifies first, and that which penetrates the seams and cavities of the coal gasifies next in the combustion chamber, thus exploding the particle. The areas exposed to oxidation are thereby made greater than the surface even of sprayed liquid droplets or of coal particles. There is also an advantage due to the fact that the hydrogen content is less than that of oil. Grade 14, with 30 per cent coal and 12 per cent coal distillates suspended in pressure still oil, displayed a market advantage in an eight hours' regulation tests made in April 1919 over Mexican topped oil tested under the same conditions. The ordinary grades of colloidal fuel show heating efficiencies per million heat units substantially equal to those of standard fuel oils, as numerous regulation tests have shown. Even on a poor boiler, the poorest grade made with 38.5 per cent of anthracite rice containing before incorporation 25.5 per cent ash equalled in result the tests of handpicked Pocahontas coal on the battleship Wyoming with a modern equipment of a water tube steam generators.

Fourth, colloidal fuel may be used in the usual oil-burning installations without material modification. On the U.S.S. Gem the existing oil-firing equipment and Norman boilers were used with no substantial change. On land boilers at Greenpoint, New York, practically no preliminary mechanical adjustment was necessary. Several varieties of mechanical and steam burners have been used. If long storage is intended, the tanks may be equipped with a current-producing apparatus, and, as with heavy oils, there should be a heating coil in the tank to give the fuel a desired fluidity before pumping to the preheater and burners. Colloidal fuel, carrying up to 40 per cent of carbonaceous particles, is practically the equivalent, in regard to handling to the preheater stage, of the heavier class of fuel oils. At higher temperatures, however, such as obtain in the preheiter, it may approximate the behaviour of the lighter class of oils. The burning of liquid colloidal fuel requires simply the procedure in buring fuel oil. To use the pastes, however, it may be necessary to slightly modify the installation and increase the pressure to move the fuel to the burner. In the case of a gel which is liquefied by pumping, or which liquefies in the preheater, more pressure is apparently alone required. While at normal temperatures colloidal fuel is like a heavy Mexican oil, it handles as well as oil with the usual preheat. Colloidal fuel may be transported in tank cars and through pipe lines. The art of heating, piping and pumping heavy liquids has been solved in America.

Soil Colloids

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Introduction.

The organic and inorganic matter of the soil consists of a mixture of particles differing in size and composition. In most soils we meet series of materials in different dispersions, from the molecular and ionic dispersed solutes of the soil up to relatively coarse sand. Therefore in recent years colloid chemistry, which stresses the importance of degree of dispersion, acquired increasing importance in soil science.

As far as we know at the present, the most important changes take place in the highly dispersed portion of the soil. Since very early times the great difference that exists between the variably dispersed portions of the soil was used for classification; and soils consisting mainly of relatively coarse material were called sandy soils, while those consisting mainly of finely dispersed material were called clays. But not only in soil classification is knowledge on the degree of dispersion of soil particles of importance; adsorption phenomena, coagulation, etc., can be explained only by the rules of colloid chemistry. J. M. van Bemmelen,[8] P. Ehrenberg,[12] E. Ramann,[51-54] H. Sallinger,[56] G. Krauss,[44] J. A. Hanley,[30] M. Stortz,[67] G. Wiegner,[74-78] P. Tuorila,[70] H. Müller,[47] E. Gullay,[17] A. Mitscherlich,[46] R. Bradfield,[11] W. S. Robinson,[55] M. S. Anderson,[3] P. L. Gile,[25] S. Mattson,[45] W. H. Frey,[15] A. F. Joseph,[40] S. Odén,[48-50] H. Stremme,[68] R. Gans,[18] A. A. J. de 'Sigmond,[59-66] D. J. Hissink,[33-36] J. Alexander,[2] K. K. Gedroiz [19-23] are among those who worked on the various problems and who applied pure colloid chemistry in their investigations on soils. Literature references can be found in the works mentioned, and it seems unnecessary to repeat their results here. Moreover, many other papers deal with colloid problems in soils, but space does not permit making reference to them all.

The colloid portion of the soil can be divided into two large groups, organic and inorganic colloids. This division is based not only upon differences in chemical composition but also on differences in colloidal behavior. The inorganic colloids are suspensoids (irreversible, hydrophobic, or lyophobic colloids). The organic colloids on the other hand are emulsoids (reversible, hydrophilic, or lyophilic colloids). In other words the inorganic colloids (generally called *clay*) are highly dispersed solids, while the organic colloids (called *humus*) are finely dispersed liquids. In many respects this clay resembles artificially prepared zeolites and is, therefore, referred to as the zeolite-like part of the soil. In addition to colloid particles 100-1 mμ in diameter, clay also contains crystalloidally dispersed as well as relatively coarser particles. At the suggestion of Atterberg, the International Society of Soil Science [87] accepted the following classification of soil particles in 1913:

Mm. in Diameter	Class
20-2	Gravel
2-0.2	Coarse sand
0.2-0.02	Fine sand
0.02-0.002	Silt
0.002	Clay

According to this classification, clay comprises not only particles smaller than 100 mμ but also those all the way up to 2 μ (2,000 mμ).

The total organic matter of the soil, called *raw humus,* can be subdivided into two parts: (1) *undecomposed* organic residues of plants and animals, and (2) *decomposed* organic compounds in colloidal dispersion, *called active humus.*

The inorganic and organic colloids together form the so-called "humus-zeolite-complex" of the soil.

THE HIGHLY DISPERSED MATERIALS OF THE SOIL AND THEIR PROPERTIES.

The inorganic and organic colloids of the soil differ not only in degree of disperson, but also in chemical composition. It is impossible to separate entirely the various colloids of different chemical composition by methods now available, since their physical and chemical properties are closely allied. Some well-known compounds have been prepared from the inorganic and organic part of the soil (*see,* e.g., O. Schreiner [58]), but it is not yet evident whether these compounds have been originally present or were formed in the course of the analytical method applied.* The inorganic soil colloids are chiefly mixtures of aluminosilicates and contain, furthermore, colloidal SiO_2, TiO_2, Al_2O_3 and Fe_2O_3 as well as identified mineral constituents of colloidal dispersion as shown by P. L. Gile.[24]

The Inorganic Colloids.

The inorganic soil colloids, as before mentioned, are suspensoids which are readily coagulated by electrolytes. They are usually negatively charged and therefore adsorb positively charged cations and colloids. The charge of the

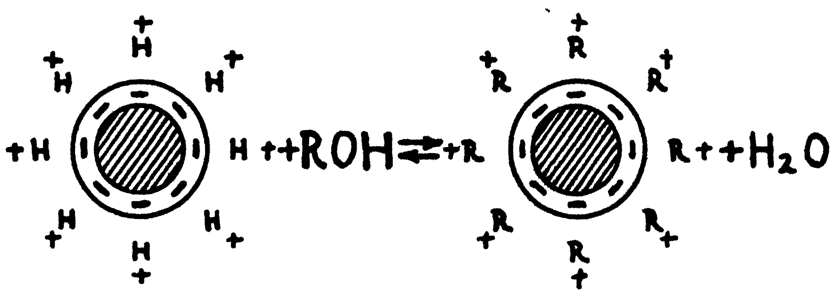

FIG. 1.

soil particles is determined by the inner ion shell on the surface of the particle, which is covered by another ion shell of opposite charge. All phenomena are connected with this exterior ion shell, as for instance adsorption (*see* Fig. 1, base exchange; and Fig. 2).

* The recent researches of The Svedberg (mainly reported in *J. Am. Chem. Soc.*) on proteins have shown that in many cases (e.g., elactalbumin) the products obtained by laboratory methods of separation are artifacts of different molecular aggregation from what occurs in nature. J. A.

The base exchange properties of soils have long been studied. T. Way[73] in 1850 described the phenomenon of base exchange and E. Ramann,[52-53] A. A. J. von 'Sigmond,[59] D. J. Hissink,[34, 36] K. K. Gedroiz[19-28] and others were pioneers in this line of science. Ramann has shown that the base exchange follows the law of mass action.

The inorganic soil colloids are very variable in their chemical composition, according to R. Bradfield,[11] W. S. Robinson and R. S. Holmes,[55] K. K. Gedroiz[28] and others. The composition is very much influenced by climatic conditions. Among the known compounds, SiO_2 and TiO_2 are always negatively charged and are readily coagulated by electrolytes, though organic colloids, for instance humus, tend to inhibit coagulation. Colloidal Al_2O_3 may be either positively or negatively charged, while colloidal Fe_2O_3 is positively charged. According to B. Aarnio[1] humus can act as a protective colloid in the coagulation of colloidal iron oxide or aluminum oxide.

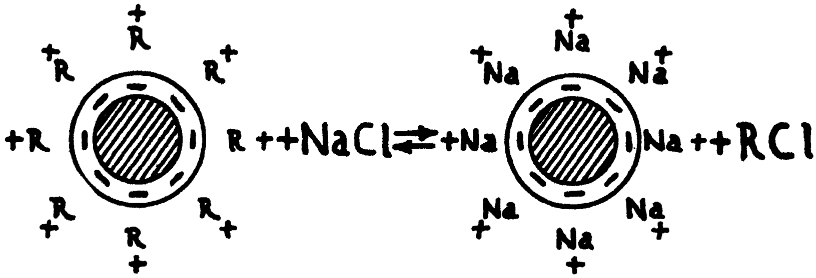

FIG. 2.

The Organic Colloids.

The organic colloids, being emulsoids, are less sensitive to electrolytes than the inorganic colloids. In the case of emulsoids the inner ion shell is covered by a thick water layer, and they become hydrated (*see* Fig. 3). Their electrical charge therefore plays no rôle, or only a small one. Their stability against electrolytes is partly due to the hydrate water.*

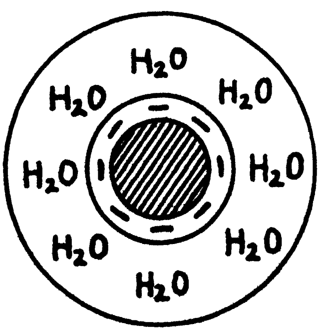

FIG. 3.

The organic colloids act as protective colloids in the soil, but, according to

* To a certain degree the negatively charged soil microörganisms can also be regarded as organic soil colloids [14, 38, 79] though their degree of dispersion is comparatively low and their quantity is very small as compared with the other colloids.

Aarnio,[1] they may accelerate the coagulation as sensitizers at certain concentrations.*

The properties of humus vary according to the climate. Under humid conditions an acid humus is formed and due to its high degree of dispersion it is leached into the subsoil. The pH of this acid humus is as low as 4 and even less. A neutral humus is formed in the steppes, is saturated with calcium and therefore coagulated. Alkaline humus which occurs in alkali soils, and which is saturated with sodium, shows a pH value of 9 or even more. According to 'Sigmond [61] the alkali-humate is very mobile in these soils.

Two opposite conceptions have been developed on the chemical composition of humus. According to A. Baumann and E. Gully [7, 29] humus contains several chemical compounds having differently dispersed particles. On the other hand, S. Odén [50] considered humus as a certain mixture of the so-called "humic acids." The former standpoint seems more justified, for in the papers of Schreiner, mentioned above, some well-known chemical compounds are described, prepared from humus.

However it is not impossible that the different chemical compounds prepared up to the present are only individual members of series of compounds, the initial ones being plant and animal constituents (cellulose, proteins, fats, lignins, etc.), while the final ones are products of decomposition (CO_2, NH_3, H_2O, H_2S, etc.). No doubt microörganisms play a great rôle in humus formation since they carry out not only the decomposition of the raw materials, but also form humus-like by-products (Waksman [72]).

The Origin of Soil Colloids and the Changes They Undergo.

Two factors are of great influence in the formation of soil colloids: climate and vegetation. From different minerals and organic materials the same soil can be formed under the same climate and vegetation; and, on the contrary, from the same minerals and organic material different types of soils can arise if the climatic conditions and the flora are different. As Ramann,[51] Glinka,[28] Kossowitz,[43] Hilgard [32] and others demonstrated, climatic conditions (humidity and temperature) and vegetation also play a prominent rôle in the formation of and in the composition of the colloidal part of the soil, their magnitude and proportion controlling the composition and dispersion of the colloids. Under a humid climate the amount of acid products will increase during the weathering processes due to the increased microbial activity and CO_2 liberation, while in arid zones neutral or alkaline products will be formed by the process of decomposition. Thus, the soil colloids formed under humid conditions are rich in humic substances and silicic acid and more or less unsaturated on account of the leaching down of the alkaline products formed by hydrolysis into the deeper horizons. On the other hand, the soil colloids formed in dry regions show a neutral or alkaline reaction since the alkaline products accumulate in one of the upper horizons owing to the high evaporation.

The decomposition products of the inorganic minerals are formed directly by the soil-forming factors (climate and vegetation), which take part in the formation of organic colloids only indirectly; for the organic materials become humus only through the influence of the soil microörganisms, the varieties and variability of which are controlled by the climate. Climate, therefore, exerts its influence only through the microflora.

* H. Bechhold has shown that while gelatin in excess of three parts per million acts as a protector to colloidal, smaller quantities render the gold more sensitive to the coagulating action of electrolytes. J. A.

The Formation of the Inorganic Soil Colloids.

Chemically the formation of the inorganic soil colloids can be considered as an hydrolysis, that is, the minerals are split into components with adsorption of water and, by reaction of these components upon one another, new compounds are formed. Accordingly soil colloids can be divided into three groups: (1) minerals still intact, in colloidal dispersion; (2) formed products in colloidal disperson (SiO_2, TiO_2, Al_2O_3, Fe_2O_3); and (3) materials of colloidal dispersion formed by the reaction of the newly generated molecularly and colloidally dispersed substances. The composition of the latter closely resembles artificially prepared zeolites.

According to some investigators, e.g., Stremme,[68] soil colloids are formed only by processes as mentioned under (3). On the other hand Bradfield[11] and Gedroiz[28] have shown that colloids synthesized from their components differ greatly from real soil colloids. Furthermore, Gile[24] proved by X-ray spectrography that in the colloidal part of the soil the presence of minerals may be demonstrated.

The Formation of Organic Soil Colloids.

The organic soil colloids are products of decomposition of plant and animal residues. The various processes taking place during decomposition are called "humification," which process, according to Ramann,[51] shows the following stages in its progress:

1. The organic origin is visible to the naked eye (peat, parts of leaves, etc.).
2. The organic origin can be seen only under the microscope: (a) the individual particles possess structure; (b) by-products of microbial and animal origin without structure.
3. The organic materials are visible only under the ultramicroscope. (a) Humus substances of low dispersion saturated with bivalent cations, and those of high dispersion saturated with alkalis. (b) Unsaturated humus substances of high dispersion.

Due to the different microflora and fauna of the different soil types, the properties of humus are very variable. In forest and peat soils where conditions are rather anaerobic chiefly acid humus substances will be formed, while in tshernozem and similar soils where aerobic microörganisms are predominant the humus substances formed are less acid. Humus in alkali soils is saturated with alkalies due to the great amount of sodium salts these soils contain; and it is highly dispersed.

Alterations of Soil Colloids.

Among the properties of soil colloids the adsorption, base exchange, acidity and degree of dispersion are most important. To study the alterations of soil colloids it is necessary to understand the interrelation of these phenomena.

Adsorption.

Since soil colloids have a negative electric charge they fix cations by adsorption. The ratio of the quantity of soil colloids and that of fixed cations can be expressed by several equations, the best known of which are those of Freundlich,[18]

$$x = K . c^{\frac{1}{p}} \tag{1}$$

where x means the quantity of cations adsorbed by 1 gram of colloids and c the cation concentration of the solution with which the colloid is in equilibrium after adsorption. K and p are constants.

The Vageler [71] formula is $$y = \frac{x.S}{x + c} \qquad (2)$$

where y is one-tenth of the ions adsorbed by 1 gram of colloids in milligram equivalents, and x is one-hundredth of the initial concentration of the adsorbed ion in milligram equivalents. S and c are constants.

According to Ramann [52-54] and his followers, who studied exhaustively the phenomena of adsorption, the properties of colloids (degree of dispersion, acidity) depend chiefly on the quantity and quality of the adsorbed cations. Ramann [52-54] and furthermore 'Sigmond [59, 60, 63, 64] and Gedroiz [23] showed that the physical conditions of soils consequently depend on the kind of cations adsorbed. Soil colloids saturated with univalent cations have unfavorable physical properties, hydrolyze greatly, are highly dispersed and show a strongly alkaline reaction, while soils saturated with bivalent cations exhibit good physical condition, have crumbly structure, their colloids do not hydrolyze and show a neutral reaction. Ramann and his co-workers also proved that not only the colloid part of the soil shows adsorption but also that of lesser dispersion. They have shown that soils do not adsorb all cations uniformly, but to a different extent. Hydrogen and the trivalent cations are bound much more strongly than bivalent and the univalent cations.

The fact that the properties of soil colloids depend upon the amount of the adsorbed cations and their proportion is of importance from the standpoint of soil science since this enables us to classify soil types if the adsorbed cations are known. 'Sigmond's investigations [64] showed that the proportion of the uni- and bivalent cations adsorbed by, and the degree of saturation of soil colloids in the different horizons, are closely related to the changes which influenced the formation of the soil. Soil colloids are usually not entirely saturated and are able to adsorb further quantities of cations. According to Hissink [85] the percentage to which the complex is saturated shows the degree of saturation. This degree can be expressed by the following equation:

$$V = \frac{100\,S}{T}$$

where S gives the adsorbed cations in milligram equivalents and T the maximum of cations which can be adsorbed by the soil complex. 'Sigmond,[66] Gedroiz [22] and di Gleria [26-27] cleared up this subject more exhaustively.

Base Exchange.

The cations fixed by the colloidal part of the soil can be exchanged for cations of other electrolytes. This phenomenon is called "base exchange," and the laws governing it have been developed by Ramann, Gedroiz,[28] Hissink [84, 86] and 'Sigmond.[59, 60, 62] They have shown that a base exchange is ruled by the law of mass action. Two factors influence the course of exchange, the first a qualitative one depending on the kind of cation, while the second is of quantitative nature and is determined by the concentration of the entering cation. Base exchange carried out with uni- and bivalent cations is a reversible process, while with hydrogen and trivalent cations it is irreversible, for only a part of the newly fixed cations can be exchanged again for other bases, according to Gedroiz [21] and Bobko and Askinasy.[10]

Acidity.

According to Biilmann [9] the proper acidity of the soil is expressed by its pH value. However, more recent investigations have shown that the different methods of pH determination give variable results and that the "true" and "apparent" pH values are greatly influenced by the treatment of the soil samples. Wiegner and Pallmann [78] concluded from their results that (1) in solutions or suspensions containing colloid materials or such of a higher dispersion only the "apparent" pH value can be determined, since the hydrogen-ion concentration measured is a complex of both the pH of the soil solution and that of the soil colloids, and (2) the pH value of soils is determined by the quality and quantity of adsorbed cations as well as by their proportion.

The pH value of soils is not only of theoretical but also of practical importance. Arrhenius [6] has shown that every plant is accustomed to an optimal pH and that the growth and yield depend greatly on the hydrogen ion-concentration of the soil.

As regards to the titratable acidity of soils, two different kinds of that acidity appear in different salt solutions according to Gedroiz,[22] Kappen [41] and Bobko and Askinasy: [10] (1) the so-called exchange acidity, which appears under influence of neutral salt solutions (KCl, $BaCl_2$), and (2) the hydrolytic acidity, observed when alkaline salt solutions are used.

Exchange acidity is a result of base exchange processes, but it is not yet clear whether the absorbed hydrogen or aluminum is set free by the cations of the neutral salt. The titrated soil solution contains in every case the amount of aluminum equivalent to the acidity; however, it cannot be stated precisely that this aluminum was adsorbed, or that it was dissolved from the colloidal portion by the hydrochloric acid (if KCl was used) nascent at the moment of hydrogen exchange (*see* Trénel [69]).

Hydrolytic acidity appears upon use of salt solutions of alkaline reaction (calcium acetate, potassium acetate, etc.). In solution these salts are split into a highly dissociated hydroxide and a slightly dissociated acid. The soil colloids fix the highly dissociated hydroxide, while the acid remains free and can then be titrated.

Coagulation.

This phenomenon of soil colloids has been studied by Ramann and Wiegner and their coworkers. J. A. Hanley [30] has shown that coagulation can take place not only in the case of materials of colloidal dispersion, but even with those of coarser dispersion. According to the results of Wiegner,[75-77] Tuorila [70] and H. Müller,[47] two kinds of coagulation can be distinguished: (1) the slow and (2) the rapid coagulation. Colloid particles possess an electrical charge and can come into contact only if the forces due to Brownian movement overcome the repelling forces due to the electrical charge. If these forces are equal or the repelling force is smaller, then slow coagulation occurs. If the colloid particles lose but their electrical charge entirely, rapid coagulation will ensue. The coagulating ability of electrolytes can be traced back to the compensation of the electrical charge of the particles, which stick together in absence of the repelling forces.*

The different cations have variable coagulating effects and can be ranged (after Wiegner [77]) as follows:

$$Fe > Al > Ca > Mg > K > NH_4 > Na > Li$$

* These attractive forces arise from the unsatisfied electronic fields of force which, to a greater or less extent appear at all interfaces. See, e.g., paper by McBain and Alexander in this volume. J. A. J. A.

Soils coagulated by univalent cations are pepticised again after influence of the electrolyte is removed, while those coagulated with bi- or trivalent cations do not practically change their degree of dispersion after the removal of electrolyte. This is of great practical importance, for highly dispersed soils of bad physical structure can thus be converted into soils of low dispersion and good physical condition. The coagulation effect of electrolytes can be accelerated by certain substances (sensitizers) or prevented by others. Humus for instance can act either way. The fact that iron precipitates in original soils only when humus has already been coagulated, is due to the protective action of the humus substance.

Utilization of the Knowledge on Soil Colloids.

Since ancient times methods have been employed in soil improvement which are based upon changes in the properties of the colloidal part in soils. The oldest of these methods is liming; its effect is due to the coagulation of the soil colloids by the calcium cation, by which the soil gets a crumbly structure. But, the coagulation of the soil colloids by treatment with lime changes also other soil properties; for instance, the acidity becomes reduced and the saturation increased. Furthermore, aeration of a crumbly soil makes possible development of a desired soil population and consequently to an enrichment of plant nutrients. Such a soil contains neutral organic matter and withstands drying. However, lime can be used successfully on acid soils only because it is insoluble in those of alkaline reaction, which can be improved by treatment with acid substances only.

Accordingly, two groups of methods can be distinguished in soil reclamation: (1) those using substances of alkaline reaction and (2) methods in which acid materials are applied.

Soil Reclamation with Alkaline Materials.

In the first group belong those in which the colloids must be coagulated, and also the acidity reduced, e.g., peat and forest soils. The coagulation in these soils is consequent on the adsorption of calcium, that is, to replacement of hydrogen by that cation; and it increases the pH value greatly. The lime requirement can be calculated from the hydrolytic acidity, for the calcium will be fixed chiefly by adsorption and consequently its quantity is approximately proportionate to the hydrolytic acidity. [Calcium is often added in the form of gypsum, "land plaster." J. A.]

The second group comprises soils in which the colloids only must be coagulated, their reaction being nearly neutral. The changes which take place during the reclamation of this type of soil have been exhaustively studied by Arany [4] and he has to a great extent cleared up the occurrences involved in reclamation of the leached alkali soils. In these soils the necessary $CaCO_3$ is *not* proportionate to the hydrolytic acidity, since the calcium does not replace hydrogen while going into solution, but replaces other cations. For this purpose di Gleria developed a method for estimating the necessary amount of calcium by determining the lime necessary to coagulate the soil on treating 100 grams of soil with increasing amounts of $CaCO_3$. Double the quantity sufficient for coagulation should be applied in practice in order to attain desirable improvement, since the solubility of $CaCO_3$ is low. The specific volumen of the soil should be taken as 2 and the lime should be calculated on the basis of a top layer 20 cm. deep.

Soil Reclamation with Acid Materials.

These substances are used primarily with alkali soils containing sodium carbonate. According to 'Sigmond,[61, 65] Arany,[5] Herke,[31] di Gleria,[26] Kelley,[42] Samuels [57] and others such alkali soils usually contain much calcium, but due to the high alkalinity it is insoluble and cannot act as coagulant. The colloids in these soils coagulate only by reducing the pH down to about 8 (di Gleria [27]).

For this purpose acids or acid-containing substances must be applied, e.g. sulfuric acid, aluminum sulfate, gypsum or sulfur. Sulfur acts slowly since it must first be oxidized to sulfuric acid by the sulfur bacteria. Gypsum has also a slow effect owing to its low solubility. Furthermore the equivalent amount of this agent is not as effective as that of sulfuric acid, sulfur, or aluminum sulfate because of the CO_2 liberated by this latter group, which also takes part in the neutralization. The necessary amount of the improving material can be obtained by a method similar to that described above.

From the work here referred to, the chemical reclamation of these alkali soils must accompany improvement in the hydrologic conditions of the area. Such soils are formed at a high ground-water level and if the salts formed during the reclamation are not removed by leaching or by lowering the water level, the reclaimed soil will become sooner or later alkaline again and of the same unfavorable structure as before.

EDITOR'S NOTE.

Besides putting the soil in what farmers call *good tilth*, proper aggregation of the soil colloids is of material assistance in helping to reduce *soil erosion*, which, according to a recent paper of H. H. Bennett of the U. S. Bureau of Chemistry and Soils (read before the First Inter-American Conference on Agriculture, Forestry and Animal Industry in Washington, D. C.), causes a loss of about 126 million pounds of plant food annually in the United States. Gullying and washing have rendered 17½ million acres in this country unprofitable for farming. The loss of humus- forming and protective vegetation (e.g. by lumbering, fire, excessive grazing), and disturbance of the soil by agricultural operations (plowing, cultivation) are conducive to losses of soil. While a well-flocculated condition of the soil is helpful in combatting these losses, it must usually be supplemented by the planting of ground-holding crops (as has been done with some dunes), by terracing (as done along the Rhine and other hilly places, e.g., in Java, and in Peru by the Incas), and by erection of soil-saving dams. In the presence of *deflocculating alkalis* the soil-carrying power of running waters may be enormously increased, and this fact seems to have left its imprint on the surface contour of many regions, particularly in the western part of the United States.

O. Tamm [*Medd. Stat. Skogsföröksamst.*, **25**, 1-28 (1929); *Proc. Internl. Soc. Soil Sci.*, **4**, 347-8 (1929)] reports that when feldspars are ground in the presence of water down to 2 to 0.2 μ, marked reactivity results. Microcline and oligoclase show alkaline reactions reaching respectively to pH 10.7 and 11.1, the decomposition products absorb water in amounts increasing with fineness of grinding, and this water is not removed by drying at 105° to 110° C., nor *in vacuo* over sulfuric acid at ordinary temperatures.

Benjamin Franklin applied land-plaster ($CaSO_4$) to a wheat field in such fashion that when the wheat grew the treated portion spelled the word "PLASTERED" in greener and taller wheat. He thus demonstrated the benefits of liming.

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The Colloidal Chemistry of the Soil

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Even a superficial examination of a clay soil will convince anyone familiar with the behavior of substances in the colloidal state, that such a soil contains some colloidal material. Schlösing [60] appears to have been among the first to isolate this fraction. By allowing aqueous suspensions of clay to stand undisturbed for long periods several distinct strata developed. The upper stratum, which never settled, was found to be made up of particles invisible under the highest powered microscope. When removed and dried this material formed a translucent, horny mass. On the basis of such experiments Schlösing concluded that the amount of colloidal material in clays was probably small, from 0.5 to 1.5 per cent. Ehrenberg and Given [24] came to a similar conclusion. They describe the sol prepared by them as more or less turbid in reflected light but rather clear in transmitted light. It was unaffected by prolonged centrifuging in a laboratory centrifuge. An ultramicroscopic examination indicated that the average particle diameter was about 140 mμ.

The Size Distribution of the Particles in Soils.

Since the last half of the Nineteenth Century many methods have been developed for making mechanical or physical analyses of soils. [*See* Wiley; [70] also Sven Odén in Vol. I of this series.] The sample was separated by various means into various groups on the basis of particle size. Sieves were commonly used for the coarse particles and sedimentation or elutriation methods for the fractionation of the smaller particles. The size classes in common use at present are shown in Table I. In all of the earlier work of the U. S. Bureau of Soils all particles having an "effective diameter" [47] of less than 0.005 mm. were considered clay. If the material between 0.005 and 0.002 is fractionated, however, it is found to be essentially silt-like in character. It has none of the characteristic clay properties. For that reason the International limit for clay 0.002 mm. seems to be much nearer the natural transition point between the classes. If the 0.005 to 0.002 fractionation is made, it should be considered fine silt and not clay. In the above classification no lower limit is placed on the diameter of the clay particle. Robinson [58] in a study of English clays found

Table I. *Size Classes Used in the Mechanical Analysis of Soils.*

Name of Fraction	U. S. Bureau of Soils	International Society of Soil Science
Fine gravel	2.00–1.00	......
Coarse sand	1.00–0.50	......
Medium sand	0.50–0.25	......
Fine sand	0.25–0.10	>0.20
Very fine sand	0.10–0.05	0.20–0.02
Silt	0.05–0.005	0.02–0.002
Clay	<0.005	<0.002
Colloidal clay	<0.002	......

that the negative logarithm of the settling velocity of the smallest particles was 7.00. Assuming the validity of Stokes' law and a spherical particle this would correspond to a diameter of about 30 mμ. Thomas [63] from a study of the vapor pressure of colloidal clay arrived at a value of the same order. Unpublished results obtained with bentonite in the author's laboratory indicates the presence of particles as small as 20 mμ. It is possible of course that the range extends even into molecular dimensions but the proportion of these very fine particles must be very small as practically all of a clay sol can be retained by an ultrafilter.

Since the classic work of Odén [47] on the determination of size distribution in clay suspensions by means of the automatic recording balance numerous other studies have been made to substitute this more élite method for the old mechanical analysis. All but the more recent of these studies have been considered by Odén in the reference cited above. An inherent error in the automatic balance method which seems to apply to most of the other methods based on sedimentation velocity, has been pointed out by Crowther and Coutts [21] and discussed in detail by Keen.[34] Currents set up because of density differences in the liquid under the balance pan and that at the sides and above the pan, interfere with the free vertical fall of the particles. No way has yet been found for getting around this difficulty. This error does not appear in the pipette method developed independently in somewhat different form by Robinson in Wales,[54] Krauss [38] in Germany and by Jennings, Thomas and Gardner [31] in the United States. Because of the simplicity of the technique and of the apparatus required, this method is being used more widely than any other. The most serious objection to it and to all gravity methods is that they are not applicable to particles in the colloidal range of sizes, i.e., particles much under 500 mμ in diameter. Odén [48] found for example that 69.1 per cent of an Ancylus clay was made up of particles between 14,000 and 340 mμ diameter. The average diameter of the 30.9 per cent remaining in suspension was determined by means of the ultramicroscope and found to be 200 mμ. If, as seems probable, the smallest particle in the suspension had a diameter of 20 mμ and the largest particle 340 mμ this average of 200 mμ would be in very serious error. The specific surface of the deposited fraction determined as accurately as possible by the automatic balance method was only 1.62×10^6 cm.,^{2} while that calculated for the undeposited fraction was 3.43×10^6 cm^2. When we consider that 1 gram of clay made up of particles 20 mμ in diameter has 17 times as much surface as 1 gram of the 340 mμ fraction it is quite clear that a small error in the determination of the amount of the smaller particles may cause a very large error in the determination of specific surface of the sample, and that an accurate determination of specific surface of a clay sample from its size distribution is impossible without the use of centrifugal force. The centrifugal methods developed by Svedberg * [61] and his students have not yet been applied to soils. In all of the size distribution methods used the clay particles are assumed to be spheres. Evidence to be considered later indicates that they are made up partly, if not largely, of plate-like particles which would give a particle o fa given weight a much greater surface.

The greatest single source of error in estimating the size distribution of a soil lies in the methods of preparing the sample for the analysis. Under natural conditions soil particles exist to varying degrees in the form of secondary aggregates. These aggregates vary widely in their stability. Mechanical shaking is sufficient to break some of them down but complete dispersion, that is, the

* *See also* paper by The Svedberg in Vol. I of this series.

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breaking down of all aggregates into unit particles, can usually be obtained only by a combination of rather drastic mechanical and chemical methods. As a result of improvements in the dispersion methods recent analyses of a given soil often indicate twice the content of colloidal material shown by the earlier analyses. There is still, however, wide variation in the efficiency of the dispersion methods in use, none of them apparently being suited for all types of soil.

Physical Properties of the Colloidal Material Extracted from the Soil.

The development of continuous flow centrifuges capable of developing a centrifugal force of 40,000 times gravity made it possible to separate the colloidal fraction from soils in sufficient quantity for studying its physico-chemical behavior. The method in common use at present was developed independently in essentially the same form by Moore, Fry, and Middleton [46] and by Bradfield.[11] The soil, fresh from the field if possible, is vigorously agitated for several hours, with from 3 to 5 times its weight of water. The coarser particles are removed by settling for from 1 to 10 days. The material in suspension at the end of the settling period is siphoned off and passed through the centrifuge at a rate sufficient to deposit inside the bowl of the centrifuge all of the non-colloidal material. The colloidal fraction which emerges can be concentrated by either passing it through the centrifuge a second time at a much slower rate [11] or by means of Pasteur-Chamberlain filters.[46] If carefully prepared and if the electrolyte content is sufficiently low sols prepared in this way will remain in suspension almost indefinitely. If allowed to become air dry this material is very hard and brittle. Its binding power when mixed wth sand, formed into briquettes under high pressures then dried carefully to avoid cracking is higher than that of portland cement. These briquettes crumble, however, when remoistened. This is due to a hysteresis in the drying-rewetting curve. Drying of colloidal clay leads to the formation of secondary aggregates which may be as difficult to disperse as those in the original soil. The forces responsible for the formation and stabilization of these structural units are not clearly understood. As the film of water separating the particles become thinner its cohesive force will probably cause an orientation of the platelike particles, pulling them from the random position maintained by Brownian movement in the sol into a more compact unit in which the flat surfaces will be brought very close together. The compressed film of adsorbed air formed between these oriented plates on thorough air drying, probably tends to retard the rewetting and thus helps to preserve these aggregates.

Shape of clay particles. Le Chatelier [38] thought that the plasticity of clays was due to the presence in them of a large proportion of platelike particles. If a colloidal clay suspension is swirled rapidly, scintillating stream lines can usually be observed. If such an oriented sol is examined with polarized light a double refraction is observed.[40, 72] An electric current either alternating or direct can produce a similar double refraction. This double refraction can be observed only when the sol is subjected to some force capable of orienting the particles. The fact that clays can be oriented by all of these means seems convincing evidence that they contain particles which are much larger in one (rods) or two (plates) dimensions than in the third. A careful analysis of their optical behavior seems to indicate that the particles are plates rather than rods. Alexander [1] quotes Wherry who termed such substances two-dimensional colloids.

In the last decade soil colloids have been subjected to X-ray analysis by Wherry, Ross and Kerr,[66] Hendricks and Fry.[29] Kelley, Dore and Brown [35] and others. Almost every sample studied was found to be made up predominantly of material in the crystalline state. Kelley, Dore and Brown regard the unit crystal as cubical even in the bentonites, which Ross and Shannon [56] regard as distinctly lamellar. The X-ray diffraction patterns are often not as sharp as might be wished for. By comparing the patterns of a wide range of soil colloids with supposedly pure clay minerals, Hendricks and Fry claim that montmorillonite-beidellite, Ordivician bentonite and halloysite are the common mineral constituents of soil colloids. Bauxite was found in two samples. The primary soil minerals such as micas, feldspars, and quartz were not found in the colloidal fraction. This indicates that the colloidal material is formed not as a result of the mere reduction in size of the original mineral with alterations due to weathering on the surface of the particle but to a secondary synthesis from the degredation products of the primary minerals.

Soil-Water Relationships. As affected by high temperatures. The colloidal fraction of soils is always more highly hydrated than the non-colloidal fraction. Drying to 110° C. usually results in a loss of from 8 to 12 per cent depending of course on the vapor pressure and temperature at the time of air drying. Drying to 110° C. does not, however, result in any serious irreversible change in the material. When heated, however, to temperatures of from 400° to 600° C. an additional loss of from 5 to 10 per cent in weight is obtained. The removal of this last water causes a complete and irreversible loss of all typically colloidal properties.[18] Kelley, Dore and Brown [35] find that bentonitic clays can be heated to 350° C. without any great change in their base exchange capacity or X-ray diffraction pattern. Heating above 700° C. caused, however, an almost complete loss in exchange capacity and an alteration in the X-ray pattern. The capacity of the natural zeolites to exchange their bases with those of neutral salt solutions was greatly reduced at even 350° C. This is strong evidence that the colloidal substances responsible for the base exchange reactions of clays are not of the same general type as the natural crystalline zeolites. The X-ray diffraction patterns are also very different.

As affected by low temperatures. When an aqueous soil suspension is subjected to temperatures slightly below freezing, — 1.5° C., in a dilatometer a certain amount of this water will freeze. The amount of freezing can be calculated from the increase in volume observed. If the temperature is then lowered to — 78° C. or lower an additional amount of freezing occurs but a considerable fraction of the water remains unfrozen even at the lowest temperatures.

On the basis of these differences, Bouyoucos [8, 9] divided the soil water into 3 classes: (1) free water, which freezes at 0° C. or slightly below, (2) capillary absorbed water, which freezes when the temperature is lowered from the first point of freezing to — 78° C. and (3) chemically combined water, which cannot be frozen at —78° C. The free water only was considered a solvent for soluble substances present in the system. Parker [50] found, however, that sugar or alcohol solutions were not concentrated by mixing them with dry soils and hence that the "unfree" water was really acting as a solvent.

Recent studies of the vapor pressure of soils at different moisture contents by Odén,[48] Thomas [63] and by Puri, Crowther and Keen [52] yield smooth curves over the entire range of moisture contents and hence fail to justify any of the numerous attempts to divide the moisture of soils into distinct classes. The curves of Puri, Crowther, and Keen are of the sigmoid type with the inflection point at about 50 per cent humidity.

Heat of wetting. If water is added to a colloidal clay dried at 105° C. a hissing sound is heard and considerable heat is evolved. This heat of wetting of clays has been studied by Mitscherlich,[45] Anderson,[2] Bouyoucos [9] and others.

Mitscherlich pointed out that the amount of the heat evolved was a function of (1) the specific surface of the soil and (2) the specific adhesive attraction of the soil surface. Anderson found that the heat evolved by the non-colloidal constituents of the soil was usually negligible in comparison with that evolved

TABLE II. *Summary of Properties of a Series of Colloidal Clays*
Data of Anderson and Mattson.[3]

Property	Fallon	Sharkey	Marshall	Susquehanna	Sassafras	Norfolk	Aragon
Molecular ratio—SiO_2/R_2O_3	3.62	3.11	2.73	1.99	1.85	1.60	.55
Specific gravity in H_2O	2.766	2.718	2.627	2.715	2.748	2.708	—
Av. diam. of particles—$m\mu$	102	91	106	141	128	129	—
Surface M^2/g.	21.3	24.2	21.5	15.7	17.0	17.1	—
No. of particles/g. $\times 10^{-12}$	680	960	613	263	335	322	—
Heat of wetting, Cal./g.	17.5	16.3	14.6	5.3	9.8	7.6	8.0
H_2O absorbed over 30 per cent H_2SO_4 g./g.	.178	.160	.130	.052	.114	.084	.089
Moisture equivalent—per cent	120	94	72	67	62	62	—
							(Bentonite)
Vol. in H_2O—cc./g.	2.5	1.9	1.8	2.0	1.8	1.8	9.0
Relative viscosity of 2 per cent sols	1.33	1.14	1.23	1.27	1.33	1.12	—
Exchangeable Ca + Mg + Na + K, millieq./g.	1.08	.69	.53	.09	.23	.09	—
pH	8.2	6.8	7.1	5.6	5.7	5.3	—
Organic matter—per cent	1.79	3.83	7.94	1.86	1.88	2.18	5.96

by the colloidal material. Because of this fact Bouyoucos [10] proposed that the colloid content of a soil be defined in terms of its heat of wetting. A study of the heat evolved by a large number of soil colloids of widely varying origins and chemical compositions by Anderson shows that it may vary from 4.5 to 17.6 calories per gram. (*See* Table II for more complete data.) The content of colloidal material in a soil can be estimated with a fair degree of accuracy, however, from the heat of wetting of the soil and that of some of the colloidal material extracted from the soil by the so-called ratio method:

$$\text{Per cent of colloidal material in soil} = \frac{\text{heat of wetting per gram of soil} \times 100}{\text{heat of wetting per gram of colloid from the same soil}}$$

The values obtained by this method are usually in fair agreement with those obtained by other adsorption methods.

Chemical Composition of the Colloidal Fraction of Soils

The chemical composition of the colloid fraction of soils seems to be largely determined by the environment under which it was produced and is largely independent of the nature of the parent material. The material carried in solution by river waters from the humid regions contains on the average, according to Clarke [19] a higher proportion of silica, alkali and alkali earth metals than the parent material and a lower proportion of the sesquioxides. Water from the tropical rivers is even richer in organic matter and in silica than that of the temperate regions. The residue left in the soil must therefore be richer in the sesquioxides than the parent material.

Analyses of a series of colloidal extracts from Missouri soils is shown in Table III. The soils from which these colloidal fractions were extracted represent diverse types with respect to origin, topography, age and source of parent material. They were, however, all apparently subjected to approximately the same climatic conditions. They are remarkably uniform in their content of SiO_2, Al_2O_3, Fe_2O_3 and combined water. These four substances usually make up over 90 per cent of the colloidal fraction of inorganic soils.

The analysis of Robinson and Holmes [55] of the colloidal fraction from 45 different soils from different areas of the United States show of course a wider variation. Silica varies from 31.84 to 55.44 per cent, Al_2O_3 from 16.42 to 38.28 per cent, Fe_2O_3 from 4.66 to 16.67 per cent and combined water from 3.33 to 16.56 per cent.

The Relation Between Chemical Composition and Physical Properties.

Joseph and Hancock [33] analyzed the clay fraction (particles less than 2 μ in diameter) from a number of soils most of them from Africa. The ratio of silica to alumina varied from 2.11 to 7.67. The clay with the smallest ratio was a non-plastic, nearly pure kaolinite while the one with the largest ratio was from an extremely plastic bentonite which possessed colloidal properties to an "exaggerated degree."

It has long been known by the practical agriculturist that the clay soils of the tropics were very different from those of the humid temperate region. A soil containing 50 per cent or more of clay in the humid regions usually drains very slowly and cannot be plowed without "puddling" for several days after a very heavy rain. The red soils of the tropical region with a similar content of colloidal material can be plowed within a few hours after a heavy tropical downpour. Such non-plastic porous clays are invariably found to be of the lateritic type. With high rainfall and high temperatures coupled with a luxuriant plant growth the weathering processes are greatly intensified. In extreme cases silica is removed almost completely and the resulting soil, called laterite on account of its brick red color, is made up almost exclusively of hydrated sesquioxides.

A number of other important physical properties of clays have been found to be closely correlated with their silica-sesquioxide ratios. Parker and Pate [51] observed a close relation between both the heat of wetting and the exchangeable base content of clays and this ratio. Mattson [41] found that the electrokinetic potentials of soils high in silica were much more stable when treated with methylene blue than were lateritic clays. The latter were always negatively charged but their content of exchangeable cations was small and a very small amount of a highly adsorbed polyvalent cation was sufficient to reverse their charge.

Anderson and Mattson [8] have also observed a significant correlation between the silica-sesquioxide ratio of a series of soil colloids and (1) their capacity to absorb NH_3 and malachite green, and (2) the calories of heat evolved on wetting the oven-dry clay (Table II). In a recent paper Baver and Scarseth [6] have shown that clays having a higher proportion of silica when saturated with hydrogen ions form stronger acids.

These investigations of clays of very diverse origins furnish convincing evidence that there is some sort of general relationship between the silica-sesquioxide ratio of clays and their colloidal behavior. The values for individual samples having the same ratio may vary appreciably, however. This is probably

due to differences in the nature of the chemical combinations existing. But little is known on this subject, however. Geologists were formerly prone to consider kaolinite, $Al_2O_3.2\,SiO_2.2\,H_2O$, as the characteristic clay mineral. Any excess SiO_2 above that required to unite with the alumina to form this compound was considered as "free." It is now known, however, that kaolinite is comparatively rare in soil colloids. They seem to be made up predominantly of minerals of the montmorillonite, beidellite, or halloysite types. The X-ray studies cited above seem to be conclusive evidence also against the idea formerly held by many that the colloidal fraction of clays was made up predominantly of an intimate amorphous mixture of the oxides of silicon, aluminum and iron. That small and perhaps significant quantities of these substances exist in the form of the separate oxides is not improbable, however, and may account for the fact that the correlation between the physicochemical behavior of soil colloids and their silica-sequioxide ratios is not as close as might be expected. It is well known for example that free silica does not possess the same capacity for readily exchanging its adsorbed cations with those of neutral salts, as silica combined with alumina. It is very likely, therefore, that a soil colloid which contained considerable amounts of free silica would differ considerably from one in which all the silica was present in an alumino-silicate combination. It is therefore impossible to predict with any degree of accuracy the magnitude of any of the physico-chemical constants of clays on the basis of their silica-sesquioxide ratio alone.

Chemical Reactions of Colloidal Clay.

Reaction with Water. *Hydrolysis.* Thus far we have confined our attention largely to the constituents of clay which are present in largest amount and which go to make up the colloidal anion. Our table of analyses of clays (Table III) shows, however, that they contain various amounts of alkali, and alkali-earth metals which total on the average almost one equivalent of these

Table III. *The Chemical Composition of Colloidal Clay.*

Soil	H_2O 105°C.	Volatile Matter	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	MnO_2
Memphis	10.60	11.76	50.00	28.21	3.53	1.14	1.84	1.68	.600	.056
Robertsville	10.86	13.38	49.81	29.23	3.72	.94	1.51	1.25	.000	.018
Boone D	11.28	12.47	48.77	29.90	4.05	.23	1.37	.80	.120	.007
Boone C	12.30	11.88	50.54	28.86	4.45	.73	1.42	1.01	.071	.028
Clarksville	12.66	11.34	51.34	28.00	4.53	.29	1.54	1.25	.301	.021
Wabash	12.58	11.16	50.11	24.51	3.39	1.75	2.41	1.87	.602	.027
Sharkey	12.83	11.51	52.78	24.19	4.73	1.23	2.56	1.63	.854	.023
Bates	12.46	12.43	51.18	25.59	5.17	.99	1.80	1.34	.318	.025
Putnam B. F....	12.17	13.37	50.22	27.65	4.74	.92	1.52	.85	.449	.014
Marion	12.44	11.83	52.15	26.53	5.51	.44	1.75	1.06	.302	.018
Cherokee	10.69	14.09	48.79	30.42	3.80	.35	1.29	1.03	.555	.017
Average	11.90	12.29	50.11	27.55	4.33	.82	1.73	1.25	.379	.023
Av. ratio (Molecular) ..			3.1	1.						

cations for every molecule of alumina. The colloidal behavior of clays is greatly influenced by the nature and amount of these cations. For the present let us consider a clay to be a complex colloidal salt of an aluminosilicic acid which in the humid temperate region would have the average composition $MO^{+}[Al_2O_3.3(SiO_2)XH_2O]^{-}$. The alumino-silicic acid would, of course, be a very slightly soluble and comparatively weak acid. If a salt of such an acid were ground until its particles were of colloidal dimensions and then placed in water we would expect some hydrolysis, or a partial replacement of

the Ca, Mg, Na and K present on the surface of these particles by the hydrogen ions of the water. It is well known that many freshly powdered minerals will show an alkaline reaction with phenolphthalein after being shaken with distilled water. If now this alkali freed by hydrolysis is leached away as it is under natural conditions the residue will gradually become more acid. The replacement of the alkali and alkali-earth metals by hydrogen ions under natural conditions is favored by the presence of H_2CO_3 which greatly increases the concentration of the hydrogen ions. The large area of acid soils found in the humid temperate region are formed largely as a result of this type of reaction. For such soils the extent to which the basic ions have been replaced by hydrogen becomes a measure of the relative age and impoverishment of the soil.

Electrodialysis. The replacement of bases from soil colloids by hydrogen ions can be obtained much more rapidly and much more completely if the ions liberated are removed continuously by means of an electric current.[12] The colloidal clay is placed in the middle section of a three-compartment cell between membranes which are permeable to the simple ions split off from the colloidal particle but impermeable to the colloidal clay ions themselves. The outside compartments are filled with distilled water. Suitable electrodes (platinum for anode, nickel for cathode) are placed in these outside compartments near, but not touching the membranes and a direct current potential of 100 to 200 volts is applied. The cations accumulate in the cathode chamber in the form of their hydroxides. The amount of acid accumulating in the anode chamber is usually very small, the cations coming almost exclusively from the colloidal clay anions which migrate to the anode membrane and accumulate there since they are too large to pass through. Only a fraction, usually from 25 to 50 per cent of the total bases present can be readily removed by electro-

TABLE IV. *Analyses of Electrodialyzed Colloidal Material from a Series of Clays.**

	Putnam	Putnam + H_2O_2	Susquehanna	Boone	Sharkey	Rock River Bentonite	Cheyenne Bentonite	Finest Cheyenne Bentonite
Loss on ignition	17.75	17.60	19.35	17.78	17.31	16.36	17.97	18.94
SiO_2	47.84	47.86	45.66	45.73	50.58	57.01	57.15	56.25
Al_2O_3	23.75	23.11	22.68	23.57	20.21	20.58	18.37	19.03
Fe_2O_3	7.62	8.25	8.14	9.90	6.98	3.61	3.00	2.97
FeO	.29	.08	.31	.23	.31	.09	.09	0.12
MnO	.02	.nd	.01	.02	.03	.01	.00	.00
TiO_2	.52	.52	1.02	.48	.54	.12	.29	.22
CaO	.11	.08	.10	.08	.10	.11	.14	.08
MgO	1.49	1.22	1.95	1.14	2.03	1.94	2.86	2.59
K_2O	1.16	1.20	.70	.72	1.44	.02	.02	.02
Na_2O	.07	.05	.05	.10	.11	.02	.00	.02
C	.977	.184	.667	.566	.591	.055	.198	.073
P	.04	.13	.07	Trace	Trace	Trace	Trace	Trace
S	.014	.010	.014	.015	.025	.019	.005	.011
Sum †	100.67	100.11	100.05	99.77	99.67	99.89	99.90	100.25
$\frac{SiO_2}{Al_2O_3}$	3.42	3.52	3.41	3.28	4.24	5.30	5.28	5.01
Non-exchangeable bases. Milliequivalents	104.9	91.0	117.6	78.4	139.3	102.0	148.4	133.4
Exchangeable cations (approximate)	70.	75.	80.	70.	80.	90.	100.	110.
$\frac{\text{Exchangeable}}{\text{Non-exchangeable}} \times 100$	42.6	45.2	40.0	47.0	36.5	46.8	40.3	45.0

* Clays prepared by R. Bradfield. Analyses by C. J. Schollenberger.
† Carbon is included in loss on ignition.

dialysis. This is shown by the analyses of a series of colloidal clays electrodialyzed by the author and analyzed by C. J. Schollenberger. (Table IV.) The calcium and sodium are almost completely removed from all samples. The potassium and magnesium are more firmly held however. These two elements may be able to replace each other to a certain extent in the interior of the particle, for often when the potassium content is high the magnesium is somewhat lower.

The amount of cations which can be replaced from soils by leaching with neutral salts is very closely related and in most instances identical with that removed by electrodialysis.[12, 42, 71] Because of this fact that a certain rather definite proportion of the total cations can be readily removed by such means while the remaining fraction is much more firmly held, soil chemists have divided the bases in soil colloids into two groups: (1) exchangeable and (2) non-exchangeable. The exchangeable ions are considered held in the surface layers of the crystalline particle by primary valence forces. They can be removed only when another ion is substituted for them. The exchange or absorption always involves equivalent quantities. The failure to observe a stoichiometric relationship in some of the earlier work was due usually to the failure of the analyst to consider all of the cations present. The hydrogen ion was frequently overlooked. Consequently if an acid soil containing a rather high proportion of exchange hydrogen ions were leached with a neutral salt and the leachings analyzed for only the basic ions apparently more base was absorbed than exchanged. The laws governing the exchange of ions between clays and neutral salts will be discussed later.

Let us now consider the properties of the hydrogen "saturated" clay produced by electrodialyzing until detectable amounts of bases no longer appear in the cathode chamber. If such a clay is allowed to deposit on the anode membrane, the clear water in which it had been dispersed will be found to be approximately neutral, while the clay paste itself may have a pH value of from 2.0 to 3.5. All soluble acids, whose anions were capable of passing the parchment membrane, have been removed by the prolonged action of the current, and we have left in the middle chamber only acids whose anions are of colloidal dimensions. The pH value of such clay acids have been found to vary with the amount of the solid phase present, in about the same way in which that of weak acids like acetic vary with concentration.[13]

Reaction of Hydrogen Clays with Bases. When titrated with solutions of hydroxides by means of the hydrogen electrode, these colloidal clays yield titration curves resembling somewhat those of weak monobasic acids. The curves are not as steep at the inflection point as are the curves of the simpler acids, but a fairly distinct endpoint can be obtained by means of both potentiometric and conductometric methods.[14] A few typical curves are shown in Figure 1. A curve obtained by titrating an electrodialzed silicic acid is shown for comparison with the clays. They are very different in character. Silicic acid is a much weaker acid, which shows practically no buffer action in the acid region while the clays are usually well buffered at pH values of 5 to 6.5 and hence are of about the same strength as the first hydrogen of carbonic acid. If we compare the apparent dissociation constants of the two acids on the basis of the usual mass law equation:

$$\mathrm{pH} = \mathrm{pK} + \log \frac{\mathrm{Salt}}{\mathrm{Acid}}$$

We find that at the point where the acid is half neutralized and hence at the point where the $\frac{\text{salt}}{\text{acid}}$ ratio becomes equal to 1 and hence disappears in the

above equation, leaving pH = pK, that the silicic acid will have a pK value of 10 to 11 in good agreement with the accepted values, while the clay will have an "apparent pK" value of about 6.5.

The term "apparent pK" value is used because in the above treatment the clay behaves as if it were a monobasic acid, that is, only one break occurs ordinarily. (A bentonite showing two breaks is shown in Figure 1. Such clays are very rare.) A simple calculation shows however that if all the clay particles were of the minimum size usually found, a radius of 10 mμ, such a particle would have over 7,000 replaceable hydrogen ions on it in the case of a bentonite sol. The true picture of the clay then seems to be that it is an extremely complex polybasic acid, whose hydrogen ions in different positions and possibly in different groupings have somewhat different dissociation ten-

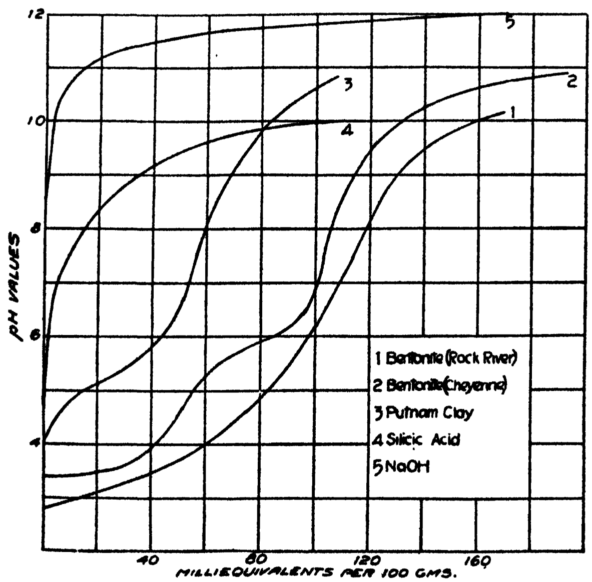

FIG. 1.—Typical titration curves of electrodialyzed colloidal clays.

dencies, but the majority of them have values of the same order of magnitude as a simple acid having a pK value near that of the "apparent pK" value.

The colloidal fraction of some of the bentonites when thoroughly electrodialyzed are of about the same strength as acetic acid. This acidity must be due to alumino-silicic acids of some sort as careful analyses of these clays show that if all of the other possible acid forming substances were combined they could account for only a small fraction of the titrable acidity measured.[15] (*See also* Table IV.) The fact that these clay acids are so much stronger than silicic acid itself indicates that they must have a very different structure. This behavior of this soil acid is evidence against the idea that colloidal clays are a mixture of colloidal silica and sesquioxides. All attempts at the preparation of artificial alumino-silicic acids having the properties of these clay acids have thus far resulted in failure.[11] The permutits which have base-exchange properties somewhat analogous to clays and which have been used as "models" by Wiegner,[67] Ganssen [25] and others differ from clays in several important respects. (1) Practically all of their cations can be readily replaced by the cations of a neutral salt solution, indicating that they have an open structure

which permits the ready entrance of the ions of the salt into the interior of the particles, while as we have seen in Table IV in the case of clays only 30 to 50 per cent of the bases present can be readily replaced by neutral salt solutions at ordinary temperatures. (2) The removal of bases from a permutit by electrodialysis results in the production of an acid resembling silicic acid more closely than the clay acids. (3) The permutits do not have the physical properties of clays. They are not as highly hydrated. The X-ray crystal patterns are very different. As cited above, Kelly *et al.*[35] have shown that their stability on heating is much less than that of the clays. The fact that clays and permutits differ in so many important respects makes it doubtful whether laws worked out on permutits can be applied to soil colloids without modification.

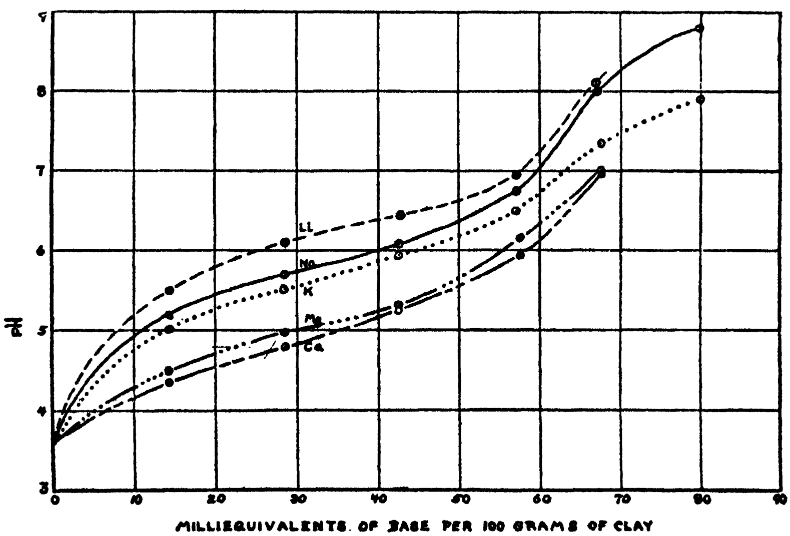

FIG. 2.—Change in reaction of clays containing various amounts of different cations.

If an acid clay is titrated electrometrically with a series of the alkali and alkali-earth hydroxide solutions of equal strengths, there are obtained a series of curves identical in general form but a fixed distance above or below each other throughout the acid range. Typical curves obtained by Baver[5] are shown in Figure 2. These measurements were obtained with the quinhydrone electrode and hence do not extend very far into the alkaline region. The order is that of the usual lyotropic series, Li > Na > K for the monovalent ions and, Mg > Ca > Ba for the divalent bases.

Clays are capable of absorbing very large quantities of bases from strongly alkaline solutions. This reaction has been studied by analytical methods with KCl—KOH mixtures by Bradfield[17] and with $CaCl_2$—$Ca(OH)_2$ mixtures by Bradfield and Cowan.[22] In both of these studies the clay was allowed to come to equilibrium with the salt-hydroxide mixtures and the clear supernatant liquid analyzed for the cation added. The curves obtained with potassium by this method flattened at a pH value of about 10 and seemed to indicate a saturation at this value. The curve obtained with the calcium mixtures showed no tendency to flatten, in fact they were steeper at pH 10 than at all except the more acid values. The absorption was later studied by the potentiometric

method used by Loeb[89] and Gortner.[28] The curves obtained by this method with sodium and potassium were of the same type as the curve obtained by Cowan with the calcium mixtures (Fig. 3). The discrepancy between the values obtained by the two methods with monovalent bases was found to be due to the fact that in the strongly alkaline solutions a considerable amount of silica and alumina were brought into solution and the cations combined with

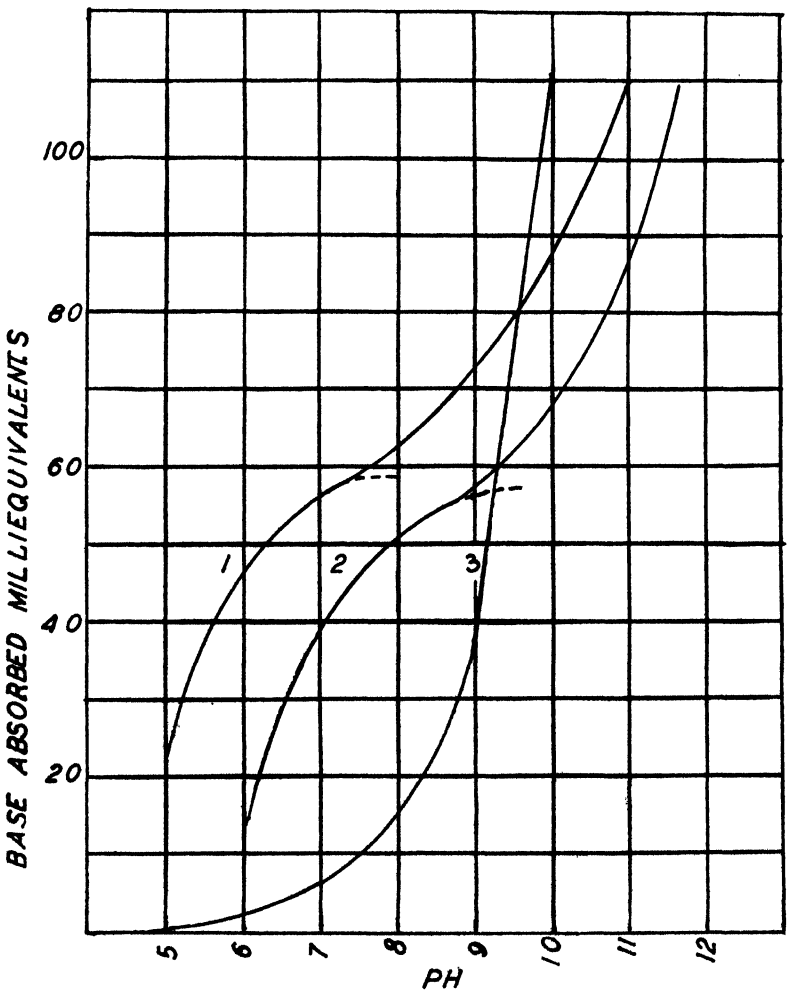

FIG. 3.—The effect of pH upon the absorption of bases by colloidal clay and silicic acid.

these substances, since they were not held by the flocculated clay, were considered "free." In the experiments with calcium similar silicates and aluminates were probably formed but they were more insoluble and hence the calcium appeared to be absorbed when the clear supernatant liquid was analyzed. The absorption of alkali and alkali-earth metals in extremely alkaline solutions seems to be due, in part at least to a break down of the clay with the formation of simpler aluminates and silicates, a reaction that is analogous to that obtained

when a clay is fused with Na_2CO_3 in preparation for a total analysis. In the case of the alkaline solutions acting at room temperature the reaction does not proceed as rapidly nor as far. The similarity between the upper half of the absorption curves obtained with clays and that obtained with silica (Curve 3, Fig. 3) tends to confirm this view. It is interesting to note on this curve that the silica does not absorb appreciable quantities of base from acid media while the clays can absorb relatively large quantities. In fact, the mid-point of the curves (dotted lines Fig. 3) corresponds very closely to the saturation capacity as determined by the usual neutral salt extraction methods and to the end-points found by conductometric or potentiometric titrations. The reaction of acid clays with bases seems then to consist of two fairly distinct processes: (1) A neutralization of the exchangeable hydrogen which is usually complete at pH values varying from about 7.5 in the case of Ca, Ba, and Mg to about 8.5 in the case of Na and Li; (2) a decomposition of the alumino-silicate minerals with the formation of simpler aluminates and silicates which in the case of the alkali metals are probably in true solution or at least in a higher degree of dispersion than the clay, while in the case of the alkali earth metals the corresponding compounds are less highly dispersed and cannot be so readily separated from the clay by physical means.

The Reaction of Soil Colloids with Neutral Salts. *Base Exchange Phenomena.* Thompson[61] in 1845 observed that when a solution of $(NH_4)_2SO_4$ filtered through a soil it exchanged a part of its ammonia for lime. Way[65] in 1852 made a more detailed study of the subject using a number of different salts. He demonstrated that the active part of the soil was the clay which he considered an alumino-silicate similar to the zeolites. Since that time hundreds of papers have been published on the subject. A good bibliography is appended to the paper of Kelley and Brown.[36] In addition to the work on soils many studies have been made in recent years of the base-exchange reactions of permutits, the synthetic alumino-silicates used for water softening. Wiegner and Jenny[68] found that the ease with which a given ion could be replaced from the permutit by another was associated with the hydration of the ion. The more highly hydrated ions like Li^+ and Na^+ were prevented by their covering of water molecules from coming as close to the permutit particle as the less hydrated ions. For ions having the same valence the electric charge on each ion is the same but the force tending to hold it to the surface of the permutit particle is inversely proportional to the square of its distance from the surface, hence the highly hydrated Li^+ ion is most easily replaced followed by $Na^+ > K^+ > Cs^+. > Rb^+$. With the divalent ions the order was $Mg^{++} > Ca^{++} > Ba^{++}$. The results agree in a general way with those cited above for clays. The extent to which the exchange reaction proceeds depends also upon the concentration of the solution. Wiegner and Jenny found that this relationship could be expressed by a modified adsorption formula;

$$(a-c) = K\left(\frac{C}{a-c}\right)\frac{1}{p}$$

in which a represents the original concentration of the cation of the salt, c its final concentration and K and $1/p$ constants. This equation differs from the regular adsorption equation in that the amount of absorption is independent of the concentration of the salt so long as the ratio of salt to absorbent is kept constant. In the experimental studies dilution had no effect upon the equilibrium. If the clay or permutit is leached with the replacing solution, the ions liberated by the clay will be removed and the reaction will go on to completion.

The extensive investigations of Gedroiz,[26] Hissink,[30] Kelley,[36] de 'Sigmond,[28] and numerous others have shown that every soil has a fairly sharply defined capacity for absorbing cations and that a knowledge of the amount and nature of these cations held in exchangeable form enables us to predict with some accuracy the properties of the soil. Mattson,[48] Anderson,[4] and Baver [6] have recently studied the effects produced by saturating the isolated colloidal fraction of various soils with different cations. Their independent work agrees on all essential points. A few of the results obtained by Baver will be cited to illustrate the general nature of the effects produced by the various cations.

Cataphoretic potential. In all of this work electrodialyzed clay saturated with hydrogen ions was used as the stock solution. Any desired degree of

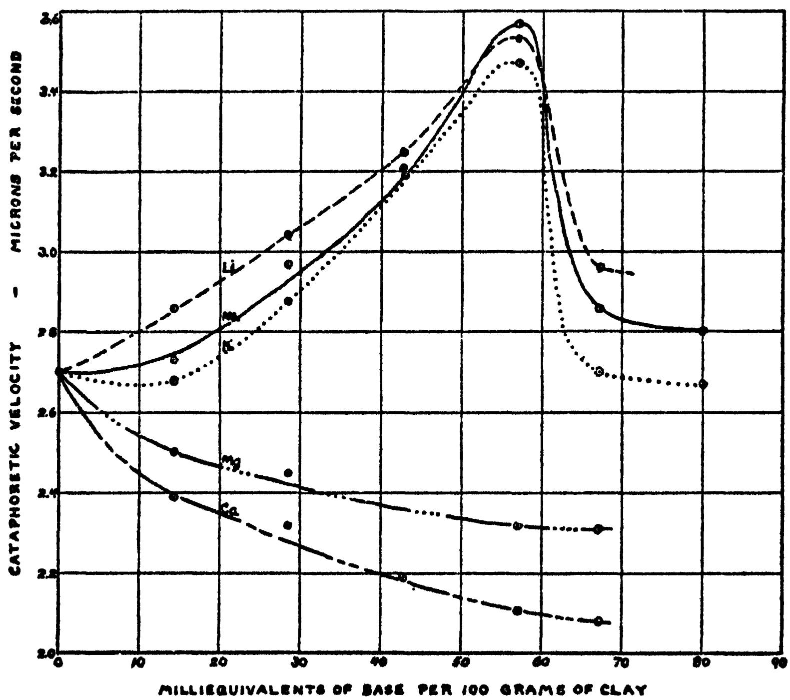

FIG. 4.—Migration velocity of clay particles affected by the amount and nature of exchangeable captions.

saturation with any base was obtained by merely adding the right amount of the cation in the form of the hydroxide. In this way no extraneous ions were introduced.

The effect of adding increments of the various bases upon the cataphoresis of such a clay is shown in Figure 4. The cataphoretic velocity was measured ultramicroscopically. Addition of the alkali hydroxides caused a gradual increase of the charge on the particles until a maximum was reached at a point near the saturation capacity of the clay. A slight excess of the free hydroxides caused a very sharp decline in the cataphoretic velocity. With the divalent bases the charge decreased from the start. Clays saturated with H^+, Ca^{++} or Mg^{++} seem to be always very near the critical potential, while the alkali metal clays are very stable over a wide range of concentrations.

Size of particle. Baver found the calcium-saturated clay particles to have a radius of about 148 mμ. The sodium clay particles were obviously much smaller but he was not able to determine their exact size with accuracy ultramicroscopically. Marshall[40] studied this same Putnam clay sol and found that the sodium clay could not be completely resolved in his ultramicroscope. The Ca, Mg, Ba and H clay particles appeared much larger and accurate counts were made. The particles were found to be of the same order as

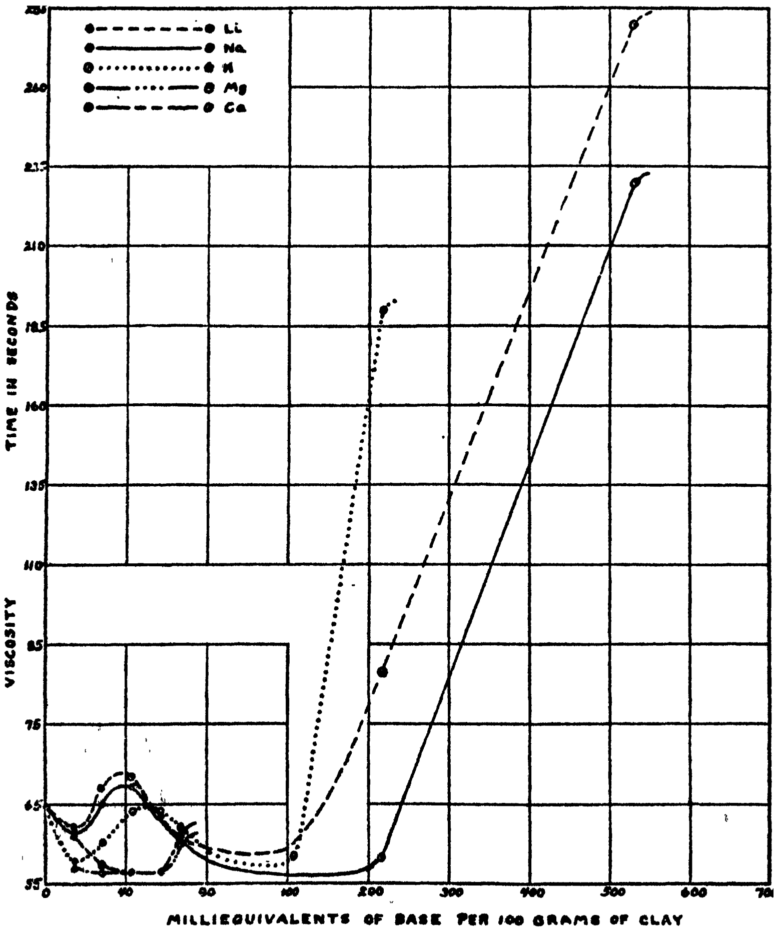

FIG. 5.—Viscosity of clay containing different amounts of bases.

reported by Baver. These particles had, according to Marshall, the appearance of compact primary particles and were very different from the loose type of secondary particle usually resulting from reversible coagulation. The Ca-clay particle is considered built up by a process of oriented coagulation. The high double refraction of these clays also seems to preclude the presence of random coagulation. If an excess of electrolyte is added, complete coagulation takes place and in this case the usual type of secondary aggregate is formed. Baver[8] measured the relative viscosity of the same sols used in the cataphoresis studies.

His curves (Fig. 5) illustrate several interesting effects. The hydrogen-clay (first point on the curve) seemed to be in a partially flocculated condition and consequently had a relatively high viscosity. The addition of the first increment of all of the bases caused a marked lowering of the viscosity, which was much more pronounced with the divalent than with the monovalent bases. With the second increment of base corresponding to about 50 per cent saturation, the values with the divalent bases continue to fall while those with the monovalent bases increase again reaching a maximum near the saturation point.

A comparison of the cataphoresis curves and the viscosity curves indicates that the viscosity is a maximum when the electric charge is a maximum. This initial increase in viscosity is unquestionably due to an increased hydration of the particles which is associated with the hydration of the exchangeable cations on their surface. As the concentration of bases is increased still further a second very marked increase in viscosity is obtained. This increase is much greater than the first and is associated with the formation of large secondary aggregates, which enclose mechanically large quantities of water. The viscosity changes observed seem to be in harmony with the fundamental idea of the Einstein equation, that is, that the changes are due to changes in the volume of the dispersed phase. In case of the initial increase the sols are highly dispersed, the increase in volume of the particle is due to ionic hydration, in the second increase the particles are beginning to flocculate, and water is entrapped within the large loosely constructed secondary particles. The curves indicate that potassium is much closer to the divalent bases in its effect on clays than is sodium.

Flocculation of Colloidal Clay.

As clays are negative sols of the suspensoid type, they are generally flocculated by very low concentrations of neutral salts. The usual valence relationships seem to hold in a general way. For example ,only a trace of a trivalent ion like Al^{+++} is required to flocculate a neutral or acid soil. Bradfield[16] found, however, that the coagulation value might vary widely with slight changes (1) in hydrogen-ion concentration, (2) in concentration of the clay sol or (3) in the nature of the exchangeable cations. An exchange of cations always takes place when the coagulation agent is mixed with the clay. The effect of hydrogen-ion concentration is most marked when other exchange reactions are prevented by the use of sols freed from all cations except H^+ by electrodialysis. If the coagulation value is determined with a series of KCl—KOH mixtures ,in which the K^+ concentration is kept constant and the pH value varied systematically by changing the ratio of KOH to KCl, two distinct critical pH zones are found; one in the acid region pH 4.0—6.0 in which only a trace of electrolyte is needed to produce complete flocculation, and a second in the alkaline region, pH 11.5 to 12.5, in which the amount of electrolyte required is unusually high. (Fig. 6.) Two distinct consecutive reactions probably take place in the coagulation in an alkaline medium. (1) The acidity of the clay itself must first be neutralized. The amount of base required for this purpose is directly proportional to the concentration of the clay. (2) A sufficient excess of electrolyte must then be added to coagulate the resulting clay salt. In the case of $Ca(OH)_2$ the amount of base required for the neutralization of the acidity of the clay constitutes from 60 to 70 per cent of the total amount required for flocculation. With KOH, however, the neutralization requires less than 10 per cent of the total electrolyte requirement. This is probably due to differences in the amount of ionization at the surface of the particle. The cataphoretic potential of the

K-clay is much higher than that of the Ca-clay and a higher concentration of electrolyte is required to bring it to the critical potential.*

If we use a natural clay sol instead of the electrodialyzed clay very different results are obtained. Using the same series of KCl—KOH mixtures as were used for the electrodialyzed clays we find our coagulation values are fairly well distributed over the entire pH range (*see* curves in Fig. 6), instead of being confined to a narrow acid and a narrow alkaline zone. This natural clay was

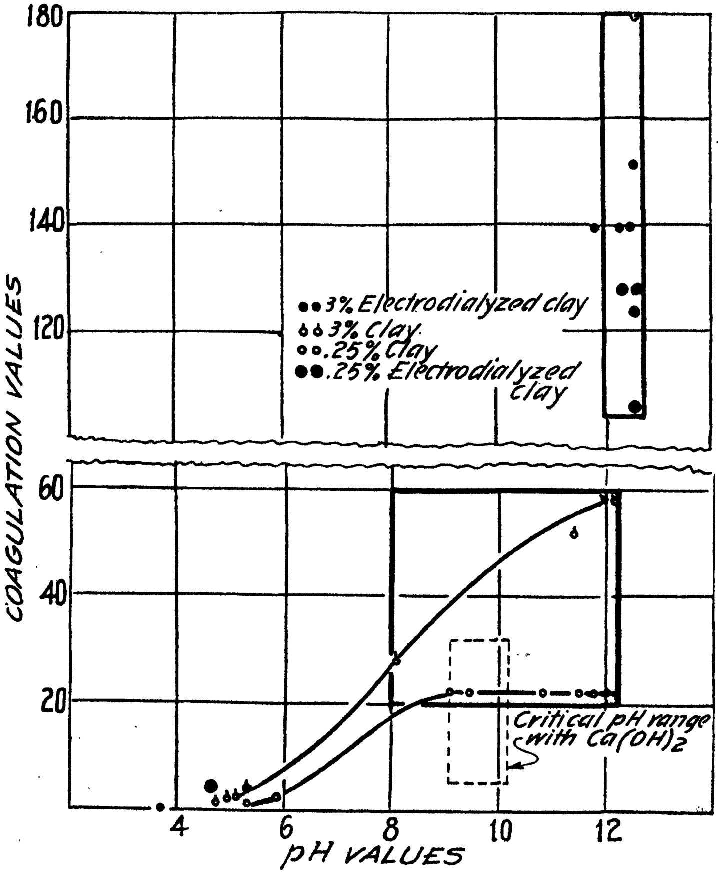

FIG. 6.—Effect of pH value on the coagulation values—clay sols before and after electrodialysis. Coagulating agents, KCl, KOH and mixtures of these solutions.

acid, about 50 per cent saturated with bases of which calcium constituted about 90 per cent of the total.

With acid clays the coagulation values with acids and neutral salts are low and practically independent of the concentration of the clay. With $Ca(OH)_2$ the coagulation value is a linear function of the concentration of the clay sol. (Fig. 7.) The amounts of $Ca(OH)_2$ required to neutralize the natural and the electrodialyzed clay (Curves D and C) are on the average about 60 per

* Regarding the general phenomena of zones of precipitation, *see* paper by A. Lottermoser in Vol. I of this series, J. A.

cent of the coagulation values. The increase in electrolyte requirement brought about by electrodialysis is just about sufficient to replace the calcium removed from the natural clay during the electrodialysis process. In other words the changes brought about by electrodialysis in the case of clays seem to be completely reversible, cations can be added to the complex or taken away repeatedly with no permanent change in properties of the sol. The waste clay sol from one series of coagulation experiments can be freed from electrolytes by electrodialysis and a second series of values identical with the original obtained.

With electrodialyzed clays and mixtures of KCl and KOH or $CaCl_2$ and $Ca(OH)_2$ very irregular curves were obtained as the concentration of clay was varied. Often a larger amount of these mixtures was required to flocculate a dilute than a concentrated sol. In many cases it was possible to obtain two

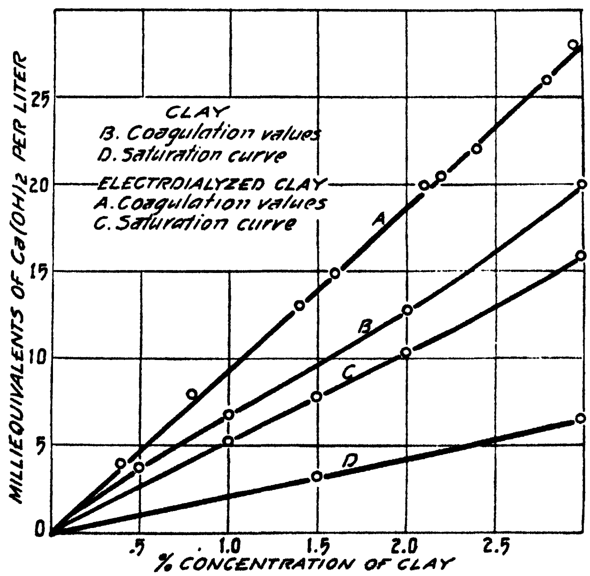

FIG. 7.—Effect of concentration of the clay sol upon the coagulation values of clay before (B) and after (A) electrodialysis. Coagulating agent $Ca(OH)_2$.

values with a single electrolyte mixture, one very low value in the acid range and a second rather high value in the alkaline region. Intermediate quantities gave a stable sol. On first sight this seems analagous to the so-called "irregular series." There is no change in the sign of the charge on the particles in this case, however. The clay is always either negatively charged or neutral. If the amount of base in salt-base mixture is insufficient to neutralize the acidity of the clay flocculation will require only a very small concentration of the cation. If, however, enough base is added to convert the H-clay into its salt a much greater concentration of the mixture is required to bring about flocculation.

Silica sols are often flocculated most readily in an alkaline medium.[11] Comber [20] claims that certain clays behave similarly. He judged the relative efficiency of the electrolytes by the rate of settling which they produced. It has been shown, however,[11] that the rate of settling is often most rapid when just enough electrolyte has been added to cause flocculation. The addition of an excess may retard the sedimentation. Comber may be right, but his evidence is not convincing. The coagulation value of clays is in general higher with

clays that have a high silica-sesquioxide ratio. The lateritic clays are usually very easily flocculated. The presence of humus usually raised the coagulation value of a clay. This is attributed to the "protective action" of the humus. The exact nature of the clay-humus relationship is not well understood.

The nature of the floccule produced by the coagulation of clay sols may vary widely with different electrolytes. Some like $AlCl_3$, $CaSO_4$ and $Ca_2(H_2PO_4)_2$ tend to produce a small but compact secondary particle which is difficult to redisperse. The alkali metals produce a much looser, more hydrated type of aggregate which can be readily redispersed by the removal of the excess electrolyte. The effect of an electrolyte upon the rate of percolation of water through a heavy clay depends more upon the type of secondary particle produced by it than upon its efficiency as a flocculating agent.

The kinetics of the coagulation of sols containing plate- and rod-shaped particles similar to those found in clays has been studied by Wiegner and Marshall.[69] They found that the Smoluchowski formula had to be modified for these anisotropic particles.

The great interest practical soil chemists have shown in base exchange phenomena in the last few years is due largely to the fact that an understanding of these reactions promises to throw much light on several of the most important problems in soil management. Such studies as indicated above have served to greatly clarify some of the problems connected with the acid soils of the humid region. The proportion of exchangeable hydrogen in the colloidal fraction, or the "degree of unsaturation with bases" as it is commonly called, is one of the best measures we have of the degree of acidity of a soil.

The soils of the arid region usually contain much more exchangeable sodium than the soils of the humid region. The low productivity of many of the so-called alkali soils of western United States has been found to be due to the unusually high proportion of exchangeable sodium in the colloidal fraction. This causes the clay to be more highly dispersed, more slowly permeable and in extreme cases almost impermeable to water and air. The removal of soluble salts by leaching with water is insufficient to reclaim such soils. In fact, if the soil is devoid of $CaCO_3$ or $MgCO_3$ such leaching may make conditions worse. To restore normal physical conditions the normal ratio of exchangeable calcium to sodium must be restored. If the soils contain a large reserve of $CaCO_3$ naturally, irrigation coupled with adequate drainage will eventually restore normal conditions.[87] The use of more soluble salts like gypsum or alum gives a quicker response. In soils containing some $CaCO_3$ the addition of sulfur which is oxidized by soil organisms to sulfate is one of the most economical ways of obtaining a normal calcium-sodium ratio in these soils. The problems connected with both the acid soils of the humid regions and the alkali soils of the arid regions seem then to be fundamentally due to a similar cause, i.e., a reduction in the proportion of exchangeable divalent bases especially calcium. They differ in that the calcium is replaced by hydrogen ions in the humid region and by sodium ions in the arid region. Their improvement calls for the same remedy, a restoration of the proper proportion of exchangeable calcium.

Gedroiz [27] has recently proposed that the soils of the world be classified on the basis of the nature of the exchangeable cations in their colloidal fraction. He has shown that fertile deep black soils, known in Russia as *chernozems* are always comparatively rich in exchangeable calcium and usually contain a reserve of $CaCO_3$. After this reserve is exhausted in regions of high rainfall the soil becomes lighter in color, its humus and sesquioxides are leached downward, forming under suitable conditions a compact horizon which in

extreme cases greatly retards drainage and aeration.* Such soils, termed *podsolic*, are found more commonly in the regions of high rainfall, are acid in reaction and are mostly covered with timber originally. Soils from the arid regions would be characterized as described above by their high content of exchangeable sodium. This plan of Gedroiz has the advantage over the climatic schemes now in vogue, that it is based on the properties of the soil itself, properties which can be readily determined on any sample in the laboratory instead of on the nature of the climatic forces largely responsible for the observed differences.

Absorption of Anions by Soil Colloids.

Monovalent anions like NO_3^- and Cl^-, most of whose common salts are rather soluble are not absorbed by soil colloids. In fact Mattson [44] finds that under certain conditions they are negatively adsorbed. It is for this reason that nitrate fertilizer should be applied only as needed for any excess will be carried away in the drainage water. The phosphate ion on the other hand is absorbed as soon as it comes in contact with the soil and only traces can be leached out with water. Van Bemmelen [7] found that if a soil were washed with acids until the exchangeable bases were removed, that it would not absorb phosphates or borates. Rostworowski and Wiegner [57] also found that permutits from which all the calcium had been removed by leaching with KCl would not absorb phosphates. Such observations led to the commonly accepted view that the phosphate ion is retained only when there is present in the soil in exchangeable form some cation with which it is capable of forming an insoluble salt.

Roszmann [58] found that while electrodialyzed colloidal clay did not absorb phosphates from alkaline solution in the absence of the divalent cations it did absorb large amounts from acid solutions, the curves showing a maximum absorption at a pH value of about 4.00.

Teakle [62] studied the solubilities of the phosphates of the metals commonly found in the soil and observed that the solubility of $FePO_4$ was a minimum at pH 3.0 which is very near the point of maximum absorption found by Roszmann. Roszmann's electrodialyzed clay contained about 3 per cent of iron in some form and it is of course possible that the retention observed by him was due to the iron. As to whether the iron and consequently the PO_4 was a part of the clay particle or a separate entity is at the present unknown.

According to Jenny [82] the surface of a permutite particle is a mosaic with both positive and negative positions, hence capable of absorbing both anions and cations. The fact that the particle is usually negatively charged is attributed to the fact that the negative points outnumber the positive points. If this is the true condition, it is difficult to understand why the simpler monovalent anions are not positively absorbed to a slight extent instead of being negatively absorbed as observed by Mattson. There is also the possibility that the PO_4^- ion may replace silica from the surface of the aluminosilicate particles. Adequate information on this point seems to be lacking.

From the information available it would seem that the retention of phosphates by neutral or alkaline soils is due largely to the formation of insoluble salts with the alkaline earth bases. The retention in an acid medium is probably due largely to iron and aluminum. A separate precipitate may form or possibly the PO_4 may replace an OH, SiO_2 or other group from the surface of the aluminosilicate particle.

* This corresponds to what is termed a pan. J. A.

The Rôle of Organic Matter in Soil Colloids.

The organic matter content of the colloidal material extracted from soils may vary from less than 1 per cent in some of the deeper horizons of infertile soils to almost 100 per cent in certain mucks. No attempt has been made in this paper to evaluate even the relative contributions of the organic and inorganic fractions to the properties of the natural product. The few attempts that have been made indicate that the relationship is by no means a simple one. Some look upon the colloidal fraction of soils as a mere physical mixture of organic and inorganic colloids and feel that there is a simple additive relation between the properties of these two fractions and those of the whole. It has been proposed, for example, that the contribution of the organic matter in a soil to its capacity for absorbing cations from neutral salt solutions could be determined by taking the difference between the capacity of the original soil and the capacity of a sample of the same soil after its organic matter had been removed by oxidation with hydrogen peroxide. Such treatment has been found [59] to decrease the absorptive capacity of some soils but to increase that of others. Odén [49] found that the so-called humic acid, prepared by extracting an organic soil with alkali then precipitating the extract with acid, had an absorption capacity of 340 milliequivalents per gram. The capacity of soil colloids will probably average less than 75 milliequivalents. The bentonitic clays have an exchange capacity of about 100 milliequivalents per gram, a value much above the average of soil colloids and they are practically free from organic matter. These examples suffice to indicate that the relation of the organic to the inorganic fractions in soil colloids is not always a simple one. The field is a most promising one for future investigations.

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Rapid Colloidal and Mechanical Analysis of Soils

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The hydrometer method [1] has been proposed as a simple, rapid and reasonably accurate method for determining the colloidal material in soils and also for making a rapid mechanical analysis of soils. From the examination that this method has thus far received, it appears that it is able to accomplish these determinations and to give reliable results.

Apparatus.

The apparatus required consists of five pieces: (1) stirring motor, (2) cup, (3) hydrometer, (4) cylinder and (5) thermometer.

The stirring motor and the cup are of the standard soda fountain type.[1] The cup has baffles inside which prevent the soil-water mixture from going into a circular motion, and cause it to be churned, thus immensely increasing the dispersion process. The motor with the modified cup, makes a most remarkably rapid and efficient method of dispersing soils. With this method the majority of soils can now be dispersed quite completely in about ten minutes as compared to 24 or 48 hours by the ordinary shaker methods.

The hydrometer has been specially made for this purpose. It was calibrated on actual soil suspension by making a mark at the points where it came to rest in the soil suspension and then evaporating the latter to dryness to determine the actual amount of material in suspension. It reads in grams of soil material per liter of water. It has been made of sufficient volume and weight to give it sensitiveness.

The special cylinder is of the 1,000 cc. type and has two marks on it, one for the use of 50 grams and the other for 100 grams of soil.

Any reliable Fahrenheit thermometer may be employed. The thermometer is needed to take the temperature of the soil suspension in order to make the proper corrections.

Procedure.

The procedure consists of placing 50 or 100 grams of soil (50 grams in case of clays and 100 grams in case of sands), based on the oven dry basis, in the cup; filling the latter with distilled water up to about 1½ inches from the top; adding 5 cc. of 1*N* NaOH and 5 cc. saturated $Na_2C_2O_4$; connecting the cup to the motor, and stirring the mixture for ten minutes. Then the cup is disconnected, the mixture is washed into the cylinder, and the latter is filled with distilled water up to the desired mark with the hydrometer in it. The hydrometer is then taken out and the mixture is vigorously shaken by placing the palm of one hand on the mouth of the cylinder and turning the latter upside down and back several times until all the soil material is in suspension. Then the cylinder is quickly placed on the table and the time is immediately

noted. The hydrometer is then placed in the mixture and readings are taken at definite intervals. Just before the reading is to be taken the hydrometer is pushed down gently in order to avoid any lagging. The reading, which is grams per liter, is divided by the weight of the sample taken, multiplied by 100 and the result is percentage of material still in suspension. The temperature of the mixture is also noted and the necessary correction made. All readings are reduced to 67° F., which is the temperature at which the hydrometer was calibrated. A change of 1° F. makes a difference of about 0.35 graduation on the hydrometer. This is only an approximate correction as it tends to vary with extreme concentrations of soil suspensions and also with extreme variations of temperature. For temperatures above 67° F. the corresponding amount of correction is added to the hydrometer reading, and for temperatures below 67° F. the corresponding amount is subtracted.

It might appear at the outset that on account of the influence on the position of the hydrometer bulb, by the varying concentration of the soil-suspension columns, and also because the density of the soil-suspension column varies from top to bottom, there must be serious errors in the results. The actual results obtained seem to show,[2] however, that the errors from these sources are very small, if any, and that the hydrometer reading tends to give an average of all the densities from the top of the soil-suspension column to the point where the soil settles out as a solid column.

Experimental Data.

By means of the hydrometer method as described above three different and distinct soil studies may be made.

In the first study the total colloidal content of soils can be determined in only fifteen minutes.[1] This is accomplished by taking a hydrometer reading at the end of 15 minutes and the percentage of material, based upon the weight of sample taken, that still stays in suspension, is supposed to represent the total amount of colloids present in the soil. This determination marks the transition point between the colloidal and the non-colloidal material of soils. The colloidal material can then be subdivided into any number of subdivisions of various size particles that one may desire.

It may appear unreasonable and incredible to claim that the total colloidal material of soils can be determined in only fifteen minutes by the hydrometer method. The claim, however, appears to be supported by several experimental facts. In the first place, soil colloids are conceived to consist of, and are defined as, that portion of the soil material which, when dried at temperature of 110° C. for 24 hours, will give off heat of wetting in water. It will be noted that this definition for distinguishing the colloidal from the non-colloidal matter of soils is based upon a recognized activity or energy manifestation of the soil colloidal material, rather than upon an arbitrary size limit of particles. It would appear that this standard has a more logical basis. According to this view, then, any portion * of the soil that is able to exhibit heat of wetting is regarded as colloidal. It has been experimentally found that all soil material formerly classed as clay and likewise the finer portion of the silt give heat of wetting. This would include soil particles as large as 0.009 mm. and even larger in some soils. Above the fine or medium fine silt there is hardly any measurable heat of wetting. All the organic matter that gives heat of wetting would also be classed as colloids. In the second place,

* Where these particles are above colloidal limits they evidently consist of gel-like aggregates of colloidal particles.—J. A.

the percentage of soil material which the hydrometer method determines as colloids at the end of fifteen minutes, corresponds remarkably closely to the percentage of soil colloids which the heat of wetting methods determine by the ratio method:[1, 8]

$$\frac{\text{Heat of wetting of original soil}}{\text{Heat of wetting of extracted colloids}} \times 100 = \text{per cent of colloids}$$

In the third place, it is possible that a certain amount of compensation of errors takes place in the hydrometer method, which tends to make the final results quite accurate.

In the second study, the hydrometer method can make a general mechanical analysis of soils[4] in only fifteen minutes. It has been discovered that if the soil particles are grouped into three main groups—sand, silt and clay or colloids—these three groups can be determined by the hydrometer method quite accurately in fifteen minutes by making only two readings, one at the end of one minute and the other at the end of fifteen minutes. The percentage of material based on the sample taken, that settles out at the end of one minute, is supposed to represent the total amount of combined sands present; the percentage of material that settles out between the end of one minute and fifteen minutes, is supposed to represent the total amount of silt present; and the percentage of material that still stays in suspension at the end of fifteen minutes is regarded as the total amount of clay or colloids present. In making these studies about thirty different soils, whose complete mechanical analysis was known, were obtained from the United States Bureau of Soils. It was found that the percentage of material that settles out at the end of one minute in the regular hydrometer method, is almost exactly the same as the percentage of all the combined sands obtained by the mechanical analysis method. If the percentage of material that settles out at the end of fifteen minutes minus the sand which settles out at the end of one minute is considered to be silt, and if the material that still stays in suspension at the end of fifteen minutes is considered to be clay or colloids, the mechanical analysis and hydrometer methods agreed quite closely in the soils whose silt content was composed mostly of the coarser size—around 0.05 mm. and disagreed rather widely in the soils whose silt content was composed of the finest size—around 0.005 mm. This might have been expected, because recent studies indicate that the finer silt has practically the same characteristics as the clay but of different degree, and should be classed, therefore, with the clay; whereas the coarser silt does not possess the same characteristics. Evidently, the hydrometer method includes in its clay or colloidal determination the finer silt but not the coarser silt; consequently, the hydrometer method would agree with the mechanical analysis method for soils with coarse silt content, but not for those with the finer silt content. In other words, the hydrometer and mechanical analysis methods agree almost perfectly in the determination of the combined sand, coarse silt and clay. Where they do disagree is in the finer silt. The mechanical analysis classes this fine silt with the coarse silt, whereas the hydrometer method class it with the clay or colloids, because it has more the characteristics of the clay or colloids. Hence, there is no radical disagreement between the two methods.

In the third study, the hydrometer method can be used to make a very detailed mechanical analysis of soils.[5] It has been found that by applying Stokes' law to the data obtained by the hydrometer method, a soil can be divided into any desired number of textural divisions. Although there may be many objections to the employment of Stokes' law in making mechanical

analysis of soils, yet it gives many fundamental comparisons of soils, and therefore has been adopted by the International Soil Congress [6] as an aid to the mechanical analysis of soils. By the combination of Stokes' law and the hydrometer method it is now possible to determine simply, quickly, and extensively the range of size and the amount of soil material that falls within this range, and thus any number of textural divisions can be made. The formula used in calculating the size of particles at the various rates of falling is shown below. The height of column and the temperature used in the calculations were 32.5 cm. and 20° C. respectively. The height is measured from the top of the soil suspension column with the hydrometer in it, to the point where the soil column is being formed:

$$v = \frac{2\,g\,d^2\,(S - S_1)\ .\ 6}{9\,nt.\ 40}$$

v = Distance in cm. a particle of d size falls in 1 minute.
g = Pull of gravity or 980 dynes.
d = Diameter of particle (mm.).
S = Specific gravity of soil (2.65).
S_1 = Specific gravity of water (1).
nt = Coefficient of viscosity of water at given temperature.
2/9 = Factor expressed in Stokes' original law.
$\frac{6}{40}$ = Used to express v in terms of cm. per minute and also diameters in mm.

According to this formula the sizes of particles that will fall at the various times in a column 32.5 cm. high and at a temperature of 20° C. are:

Time of Sedimentation	Diameter of Particles mm.	Time of Sedimentation	Diameter of Particles mm.
1 minute	0.077846	12 hours	0.0029
2 minutes	0.055050	13 hours	0.00279
5 minutes	0.034814	14 hours	0.00270
15 minutes	0.02010	15 hours	0.00259
30 minutes	0.014212	16 hours	0.0025
60 minutes	0.01005	17 hours	0.00243
2 hours	0.0071	18 hours	0.002369
3 hours	0.0056	19 hours	0.002307
4 hours	0.00502	20 hours	0.00223
5 hours	0.0045	21 hours	0.00219
6 hours	0.0041	22 hours	0.00214
7 hours	0.0038	23 hours	0.00209
8 hours	0.00355	24 hours	0.00205
9 hours	0.00335	48 hours	0.00145
10 hours	0.00318	96 hours	0.001025
11 hours	0.00303		

The foregoing figures for size of particles signify the upper limit of size of any particle that stays in suspension at any given time. For instance, at the end of one minute the upper limit of any particle that may still stay in suspension is 0.077846 mm. in diameter, at the end of one hour 0.01005 mm., etc.*

Hydrometer readings at all the various periods shown above give a very complete picture of the size and amounts of various particles, or a complete distribution curve, in any one soil. It is probably not important, however, to take all the above readings. It has been decided that the most important

* Stokes' law is based on spherical particles, and some deviations must occur with distinctly rod-like or disc-like shapes, e.g., mica. J. A.

readings are those taken at the end of 1, 2, and 15 minutes and at the end of 1, 4, 8, and 24 hours. These periods would give particles 0.077846, 0.055050, 0.02010, 0.01005, 0.00502, 0.00355, and 0.00205 mm. respectively. This would afford four divisions for silt; namely, 0.055050, 0.02010, 0.01005, and 0.00502 mm., and three divisions for clay or colloids; namely, 0.00502, 0.00355 and 0.00205 mm. Hence, both the silt and clay are divided into a greater number of division in the hydrometer method than in the regular mechanical analysis.

Unfortunately it is not possible to subdivide the sands by the hydrometer method as it is the silt and clay or colloids. For subdividing the sands, the soil suspension, after it has been used for all the necessary hydrometer readings, is poured into a 150-mesh sieve and water run over it from the faucet to wash away all the material that will go through the sieve. The sieve will retain all the coarse material up to and including fine sand. The sands retained in the sieve are then dried and passed through the different size sieves to determine the amounts of the various size sands. The very fine sand is determined by difference, for the total amount of sand is known quite accurately from the hydrometer reading at the end of one minute.[4]

Although the separation of the various sands by the above procedure may not be accurate, yet it is approximately correct. The total amount of sand, however, as revealed by the hydrometer reading, is quite correct.

Temperature affects the hydrometer readings by affecting both the density of water and the rate of settling of the soil particles. Since the soil suspensions have to stand for many hours, it is necessary that the temperature should remain constant during this period. Various devices may be used to maintain a fairly constant temperature. It has been found, however, that the most practical method is running tap water. Any kind of a container that will hold the cylinders can be arranged so that the tap water enters and runs off, thus maintaining a constant temperature.

The procedure followed in making hydrometer readings in this constant temperature bath was as follows: The soil suspensions were prepared exactly according to the methods described previously,[1] then the cylinder containing the soil suspension and the hydrometer was placed in the constant temperature bath and allowed to stand there with occasional stirring with a rod, until the contents attained the temperature of the bath. The cylinder then was taken out and the contents were shaken vigorously. The cylinder was placed on the table and the time was noted quickly. The hydrometer was then placed in the cylinder and at the end of 1 and 2 minutes the hydrometer readings were taken. It will be noted that during the first 2 minutes the cylinder was not in the constant temperature bath but in room temperature. The first two readings were taken out of the constant temperature bath because of the difficulty in placing the cylinder into the bath quickly enough after shaking it to take a correct reading at the end of 1 minute. The error that may arise from any change in temperature is slight, and corrections may be made for it. After the reading was taken at the end of 1 or 2 minutes the cylinders were returned to the temperature bath and the readings taken at the stated intervals. Before the reading was taken the hydrometer was pushed down gently to avoid any lagging. All the hydrometer readings then were reduced to 67° F. as described previously.[1] For the heavier types of soil 50 gm. should be used. but for the sands and light sandy loams 100 gm. should be employed in the test.

As stated in previous papers, the hydrometer was calibrated against actual soil suspensions. Its readings, therefore, are quite accurate. It was found very difficult to calibrate the range from 0 to 10 gm. per liter, however; and

this range is not so accurate as the rest of the range. But if 100 gm. is employed the error is very small.

The number of soils whose detailed mechanical analysis may be examined by the hydrometer method as described above, is limited mainly by the number of hydrometers and the number of cylinders that one cares to invest in. When it is considered that hydrometer readings are taken only at the end of 1, 2, and 15 minutes, and 1, 4, 8, and 24 hours, it is readily realized that a large number of soils may be started and run at the same time. It is very easy and practical to examine ten soils in about 25 hours by using ten hydrometers and ten cylinders. This is a great contrast to the time required to make a mechanical analysis of a single soil; and the important thing is that the mechanical analysis will not subdivide the soil particles into as many classes as the hydrometer method does.

The method has been subjected to very critical examination in the last two years, and so far it has proven to be a reliable method. By following the general procedure already outlined the results of nearly all soils can be duplicated almost exactly any number of times, provided the temperature is constant, or correction is made for it; that representative samples of soil are taken every time, and that the paddle to the stirring rod is in good condition. In all normal soils, this method appears to give reliable results. The only cases in which it may fail is in abnormal soil such as those which contain an abnormally high amount of carbonates, in peats and mucks or in soils which contain undecomposed organic matter, since it is almost impossible to disperse the latter.

Probably there are very few, if any, methods in soil physics which are standardized so well as this method. The hydrometer, for instance, floats and is governed entirely by physical laws with no outside disturbing factor and no personal element entering into it. The soil is dispersed at a definite speed, and at a definite time by a mechanical means.

Referring once more to the dispersing machine, there are two things that must be strictly guarded against: first, the cup must have baffles or wires on it; the second, the paddle or button to the stirring rod tends to wear out on sandy soils; when it becomes flat it must be replaced because in the flat condition it loses its stirring efficiency. In fact, the success of the hydrometer method depends upon a complete dispersion of the soil. With these two precautions, it may be said that this machine is most wonderful for dispersing soils for any purpose.

On account of its great rapidity and simplicity of manipulation, this hydrometer method is already receiving a very wide application. The various fields in which it is now being used are as follows: Soil laboratories, soil surveys, drainage and irrigation projects, highway engineering, ceramics, cement industry, oil drilling, soil forest studies, plant ecology studies, soil base-exchange studies, etc.

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The Colloid Chemistry of Wheat, Wheat Flour, and Wheat Flour Products

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Germination.

Wheat and wheat products exemplify in a remarkable degree the applications of colloid chemistry in living processes and in every-day life. When a seed is placed in the ground and provided with suitable moisture, imbibition of the wheat colloids takes place, and active growth begins. In this instance imbibition is probably necessary in order to increase the rate of diffusion through the dense gel of the endosperm so as to permit enzyme action to take place and to allow sugars to diffuse from the starchy endosperm to the growing embryo.

The Growing Period.

As the young plant develops, all of the colloidal phenomena associated with living, actively growing protoplasm may be observed. It is beyond the scope of this chapter to enter into a general discussion of the colloid chemistry of life.* There are, however, two responses which the wheat plant makes toward its environment which deserve mention.

Drought resistance is a necessary quality in many of our agricultural regions, and certain varieties of wheat are known to be well adapted to semi-arid agriculture. Plants growing in semi-arid regions may be classified into two great groups according to the method which they have evolved for drawing moisture from the soil and for retaining moisture in the cell against transpiration. The first method is characteristic of halophytes and consists in the accumulation of soluble salts and sugars in the plant sap so that the osmotic pressure of the cell sap increases as desiccation of the soil progresses. This is essentially a non-colloidal mechanism. The second method, characteristic of extreme xerophytes, consists of the building up in the plant cells of large amounts of hydrophilic colloids, thus retaining the water in the cell and drawing moisture from the depleted soil by imbibition pressure. This mechanism has reached its fullest development in the cacti, in most forms of which the osmotic pressure is a negligible factor.

Some recent investigations (Harris *et al*, 1923) indicate that the wheat plant uses both mechanisms and that the elaboration of hydrophilic colloids may play a very important rôle in the drought-resistant varieties.

Winter wheat is grown in extensive areas and is known to differ from variety to variety in its ability to resist low temperatures. Plant breeders are endeavoring to develop types which will withstand the rigor of our northern

* Many of these are treated in Vol. II which covers Biology and Medicine.—J. A.

winters. The test for winter-hardiness which has been adopted is to plant the different varieties in field plots and to note the number of plants which fail to live through the winter. Unfortunately for work of this sort, a "test-winter" does not come on the average much oftener than once in ten years, so that experiments of this type must be conducted over long periods of time in order to show conclusive results.

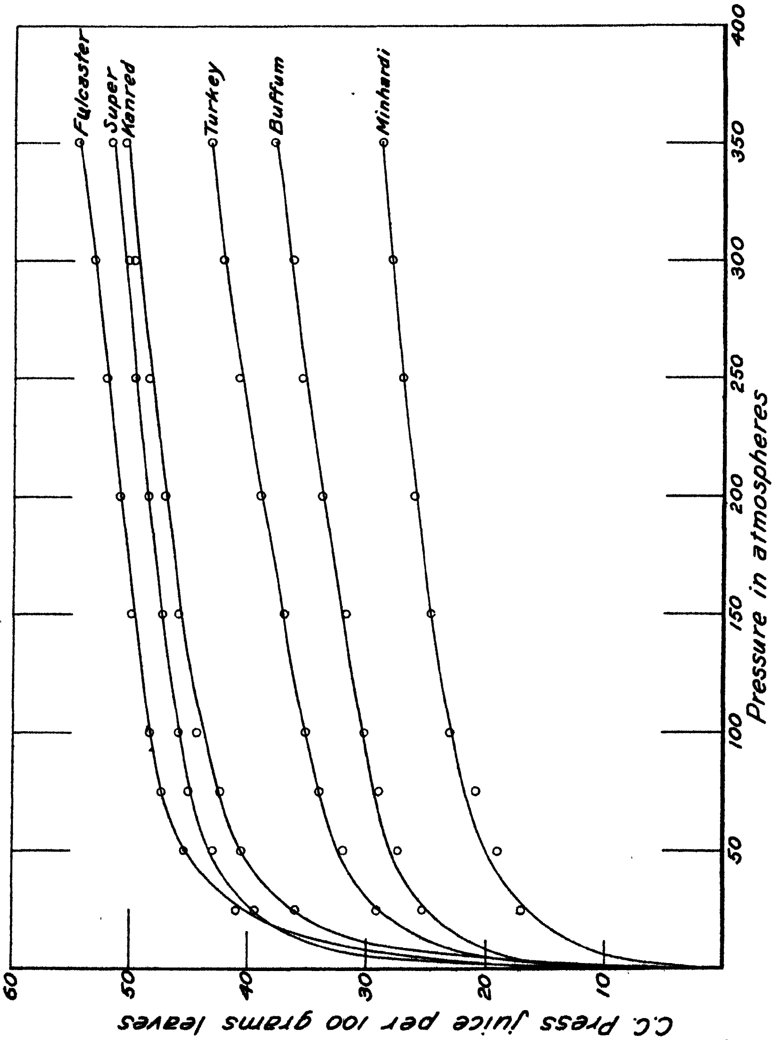

FIG. 1.—Imbibition pressure of wheat leaves in relation to winter hardiness. Minhardi is the most hardy, Fulcaster the least. The order of the curves corresponds to practical field observations of winter hardiness (after Newton).

Newton (1922, 1923, 1924) has shown that winter-hardiness in wheat is due, at least in part, to the elaboration of hydrophilic colloids which serve to bind the water and either prevent the freezing of the cell protoplasm or else prevent the disruption of the protoplasm when thawing takes place. From the data at hand it appears that protoplasmic proteins are the hydrophilic colloids responsible for the protective action. Newton has likewise shown that milligram for milligram the colloids of the winter-hardy wheats are more

effective protective colloids (as measured by gold number) than are the corresponding colloids from non-hardy or semi-hardy wheats. The amount of sap which can be expressed from 100 grams of "hardened" leaf tissue is inversely proportional to the ability of that wheat to withstand cold. Figure 1 illustrates such an experiment.

Newton and Brown (**1926**) and Martin (**1927**) have extended and confirmed the earlier studies of Newton, and while they show that the problem of winter-hardiness is not as simple as at first appeared, nevertheless their work shows that the rôle which lyophilic colloids play in the process is of primary importance.

That lyophilic colloids play a similar rôle in winter-hardiness in the animal kingdom has been abundantly demonstrated by Robinson (**1927, 1928, 1928a, 1928b**).

The Development of the Wheat Berry.

The development of the wheat berry presents an interesting study of colloidal changes. In the early stages of development the interior of the berry is filled with a milky, colloidal sol, and as development progresses this sol gradually changes into an extremely dense gel. In the very immature kernels (sol stage) we find a relatively large proportion of the carbohydrates existing in the form of reducing sugars and a very considerable proportion of the nitrogen in the form of amino acids and simple peptides (Thatcher, **1915**). As the sol becomes more viscous (late "milk" to early "dough" stage), the proportion of the carbohydrates existing in the form of soluble sugars rapidly decreases and the percentage of starch correspondingly increases. Following this stage there is a slow but progressive decrease of reducing sugars coincident with the desiccation of the kernel. Changes in the *amino acid* $\leftrightarrows$ *protein* equilibrium are apparently more gradual than in the *reducing sugar* $\leftrightarrows$ *starch* equilibrium. A very considerable proportion of the nitrogen remains in non-protein form until the later stages of ripening. Miss S. H. Eckerson (**1917**) states, "No storage protein is formed in the endosperm until desiccation begins."

Sharp (**1925**), however, has shown that protein synthesis is not necessarily dependent upon a continued and progressive desiccation, since the amount of free amino nitrogen continued to decrease in immature wheat berries (moisture content 46 to 64 per cent) which were thrashed and kept under conditions where desiccation was prevented. When, however, such kernels were frozen, protein synthesis was inhibited and in some experiments at constant moisture content there was an appreciable *increase* in free amino nitrogen. Since freezing does not usually inactivate enzymes but does destroy gel structure, it would appear that possibly the colloidal structure of the developing wheat berry is of more importance in effecting protein synthesis than are enzymatic reactions.

Soluble sugars and protein nitrogen exist in very small amounts in the fully ripened berry but reappear again if the colloids of the berry are allowed to imbibe a high percentage of water or if the gel structure has been altered by freezing (Blish, **1920**). It has been abundantly demonstrated that enzyme reactions are reversible and that at high concentration of substrate synthetic action takes place and upon dilution of the system hydrolysis occurs. In the normal development and ripening of the wheat berry the disappearance of soluble nitrogen and sugars may well be induced, at least in part, by a shifting of the enzyme equilibrium, owing to the high concentration of the solutions which exist in the extremely viscous gel.

THE STORAGE OF THE GRAIN.

Bailey (**1917, 1917a, 1921**) and Bailey and Gurjar (**1918**) have shown that the moisture content of wheat is the determining factor as to whether or not the wheat will heat in storage. They have demonstrated that wheat will not heat if its moisture content does not exceed 14 per cent and suggest that at this moisture content the colloid gel becomes either discontinuous or else so dense that diffusion through the gel is reduced to practically zero. At higher moisture contents the viscosity of the gel decreases, diffusion is accelerated, and a sharp increase in rate of respiration takes place.

Gortner (**1929**, pp. 242-243) has offered an alternative explanation for the phenomenon which Bailey observed, and suggests that at or below 14.75 per cent moisture all or nearly all of the water in the wheat berry is in the form of "bound water," i.e., in the form of adsorbed and oriented water films upon colloid interfaces. Such "bound water" would not be free to act as a solvent for the various organic and inorganic solutes present in the berry, or as a medium in which rapid enzyme actions can take place, and accordingly the vital processes of the berry would be reduced to a minimum and it would pass into a state of dormancy. An increase of 1 per cent of free water should accordingly increase metabolic activity out of all proportion to the relative increase in total water content. This is exactly what Bailey observed, for he found that an *increase* of moisture content from 14.75 per cent to 15.75 per cent increased the rate of respiration nearly 200 per cent, and a further increase from 15.75 per cent to 16.75 per cent moisture content more than quadrupled the respiration rate at the 15.75 per cent level, whereas a *decrease* from 14.75 per cent to 13.75 per cent produced essentially no change in the already low respiration rate.

THE MILLING PROCESS.

Colloid phenomena likewise enter into the milling processes. Milling is essentially the crushing of the starch-gluten gel of the endosperm between the rolls under such conditions that it is possible to mechanically separate the pericarp from endosperm material. To produce a high grade of flour the pericarp, or branny covering, should be removed as completely as possible. This can be accomplished only when the colloids composing the pericarp contain an optimum amount of water of hydration. Less than this optimum water content produces a brittle bran coat and introduces particles of bran into the flour streams. Moisture in excess of this amount decreases the friability of the endosperm and causes a loss of flour into the bran and shorts streams. The tempering process, which consists of adding water to the wheat a few hours before milling, hydrates the pericarp, rendering it tough and pliable so that it will not break to a powder upon the rolls. The time of tempering is so regulated that the moisture does not appreciably diffuse into the starchy endosperm which still retains its friability and crushes readily to a powder. It is therefore a differential hydration of the colloids of the pericarp and endosperm which is responsible for the fact that a larger yield of high quality flour can be obtained from a wheat tempered to a moisture content of 15 per cent than can be obtained from a wheat containing, as purchased, 15 per cent of moisture. In the latter case we do not have a differential distribution of the water.

THE FLOUR-MOISTURE PROBLEM.

The marketing of wheat flour presents problems involving adsorption and imbibition. Federal and state laws require that the net weight must appear

upon the package. If a shipment of flour is packed in a region of relatively high humidity and subsequently sent to and stored in a much drier region, it is possible that sufficient loss of hygroscopic moisture may take place to reduce the net weight below that stated upon the package, and yet not involve actual fraud upon the part of the packer. Bailey (1920) has presented data showing the percentage of moisture in flour in equilibrium with air at different relative humidities. This varies from 5.11 per cent at a relative humidity of 29.4 to 15.0 per cent at 80 per cent relative humidity.

Fairbrother (1929) has shown that the variation in the weight of bags of flour with relative atmospheric humidity is of importance from a merchandising standpoint and cites a case where a successful appeal was prosecuted against a conviction for short weight. He further points out that marked hysteresis is displayed when flour which has lost moisture at a low relative humidity is again exposed to the original relative humidity where it had been in equilibrium. The original equilibrium is not regained. The rate of moisture loss when flour is shifted to a lower relative humidity is rapid; the rate of moisture gain is slow when the drier flour is again placed in an atmosphere of higher relative humidity. In a typical experiment flour in equilibrium with 75 per cent relative humidity was exposed for one night to 40 per cent relative humidity. The moisture lost at the lower humidity was not regained during a 17-day exposure at the (original) 75 per cent relative humidity. "Apparently some of the particles become permanent gels and the hydration capacity is permanently reduced."

Fisher (1927) has studied the rate of drying of wheat flour, wheat starch, and wheat gluten during the exposure of flour over concentrated sulfuric acid in a closed container at constant temperature, the apparatus being so constructed that the flour could be weighed at intervals without removing it from the drying vessel or in any way disturbing the drying process. He found that when the rate of drying $(-\frac{dw}{dt})$ was plotted against moisture content (w), the rate curves were of the same type and consisted essentially of three parts separated by more or less sudden changes of directions. Down to 6 per cent moisture the curve was linear and on extrapolation would cut off an intercept, c_1, from the horizontal axis. At about a 6 per cent moisture content a sudden change in direction of the rate curve occurred, and the rate curve was again linear to about 2.5 per cent of moisture, and on extrapolation would cut off a second intercept, c_2, on the horizontal axis, c_2 being less than c_1. These two linear portions of the rate curve could be expressed by the equations,

$$-\frac{dw}{dt} = k_1(w - c_1), \quad -\frac{dw}{dt} = k_2(w - c_2).$$

Fisher notes that below 2.5 per cent of moisture the rate-of-drying curve bends slowly to the point of origin but that over this range drying is extremely slow. These observations furnish additional evidence for the idea that at least a part of the water in wheat flour is held very tenaciously in the form of oriented films on interfaces.

The problem of the great surface exposed in flour and the tenacity with which moisture is held upon such a surface likewise enters into the problem of the accuracy of moisture determinations. Nelson and Hulett (1920) point out that water may be so firmly held in surface films that it may show practically no vapor pressure. By making use of an ingenious method which enabled them to differentiate between water arising from surface films and

that formed from the decomposition of organic molecules they estimate that wheat flour showing a moisture content of 10.80 per cent when dried at 100° C. *in vacuo* actually had a moisture content of 11.8 per cent. In the light of these results it should be generally recognized that the moisture determination on a biological product is an empirical procedure and that along with the percentage of moisture one should specify the temperature, the barometric pressure, and the length of the drying period.

Gluten and Flour Strength.

The peculiar properties of wheat flour, the only one of the cereal flours which is adapted to the manufacture of yeast-leavened bread, lie in the nature of the wheat proteins. Osborne (**1907**) has characterized five proteins isolated from wheat flour: a prolamine, *gliadin;* a glutelin, *glutenin;* an albumin, *leucosin;* a globulin, and a proteose. Assuming for the moment that these are distinct entities (*vide infra*), it is probable that they all contribute to the colloidal phenomena of the flour or dough mass. We will, however, limit the following discussion to the gliadin, and glutenin, and the physical mixture of these proteins known as gluten.

Whether or not gliadin and glutenin are physically combined as gluten in the original flour, or whether this combination is formed during the process of dough manufacture is an open question, but there can be no doubt but that the gluten is responsible for the gas-holding capacity of the dough and that the structure of the dough and of the resulting bread is determined by the amount and quality of the gluten.

It is a well-known economic fact that there is a great variation in the baking quality of flour milled from different wheats. The hard spring wheats, especially those of the northern portion of our Great Plains area, yield a flour which has superior baking qualities, while the softer wheats produce flours of inferior baking quality. In order to differentiate between these qualities of flours the terms "strong" flour and "weak" flour have been generally adopted. Perhaps the best definition of strength is that adopted by a committee of the National Association of British and Irish Millers (Humphries and Biffin, **1907**). "A strong wheat is one which yields flour capable of making large, well-piled loaves; the latter qualification thus excluded those wheats producing large loaves which do not rise satisfactorily." This definition is, of course, empirical.

The chemical and technological literature is replete with investigations dealing with the question of flour strength. Almost every conceivable factor has been investigated with more or less thoroughness, and claims have been put forward by one investigator only to be overthrown by another. It has recently been recognized that strength is not necessarily the result of a single factor but is rather the expression of a group of factors, any one of which may produce undesirable weakness in the baking quality of flour. Sharp and Gortner (**1922**) express this view. "We are coming to recognize at least three classes of weak flours, i.e., (1) weakness due to an adequate *quantity* of gluten but an *inferior quality;* (2) weakness due to an *inadequate quantity* of a good quality of gluten, and (3) weakness due to factors influencing yeast activity, such as inadequate diastatic activity, acidity and amount of proteolytic enzyme, etc."

The first two types of weakness may be traced back to the gluten; the third type relates to yeast activity. That weakness of the third type may exist has been demonstrated by Rumsey (**1922**) and Collatz (**1922**). It is appar-

ently in the question of gluten *quality* that colloid phenomena are chiefly concerned, and the following discussion refers to weakness of this type.

Wood (**1907, 1907a**), and Wood and Hardy (**1909, 1909a**) were the first to investigate the relation of colloid chemistry to the strength of flour. Wood suspended strings of gluten about the size of a pencil across V-shaped glass rods in beakers containing varying concentrations of different acids and then noted the concentration at which cohesion was so far reduced as to allow the gluten to fall off the rod and disperse in a cloudy solution. He apparently used gluten from only one flour in these experiments.

In this manner it was found that gluten suspended in distilled water retained its coherence almost indefinitely, but that in solutions of hydrochloric acid as dilute as $N/1{,}000$, dispersion began almost immediately. This action increased with an increased concentration of acid up to about $N/30$, and then decreased again until at a concentration of approximately $N/12$ the gluten became "permanently coherent and much harder and more elastic, and less sticky than in its original condition."

Similar experiments were conducted with sulfuric, phosphoric, oxalic, acetic, lactic, citric, and tartaric acids, both with and without the additions of certain salts. Unfortunately, Wood does not give the necessary tabular data to permit exact comparisons; and in the curves shown, those for "acid alone" are omitted, and only certain of those for "acid + salt" are given. He finds, however, that the order in which the acids influenced the coherence of the gluten was (1) hydrochloric, (2) sulfuric, (3) phosphoric, (4) oxalic. The three remaining acids behaved quite differently, for, while dilute solutions caused disintegration, this became increasingly rapid with increasing concentrations of acid, and no practicable concentration could be found at which coherence reappeared.

Wood likewise observed that the addition of salts to the acid solution counteracted in a large measure the effect of the acid. He therefore postulated that, "the variations in coherence, elasticity, and water content, observed in gluten extracted from different flours, are due rather to varying concentrations of acid and soluble salts in the natural surroundings of the gluten than to any intrinsic difference in the composition of the glutens themselves." This view he supported in his later papers.

Upson and Calvin (**1915**) were the next to study the colloidal swelling of gluten. They employed a more exact technic than did Wood,* using the method employed by Hofmeister (**1890**) in his investigations on the swelling of animal proteins. In their experiments the gluten was first freed from starch by washing it in a stream of distilled water. It was then pressed out between glass plates to a fairly uniform thickness and, after standing for some time, was cut into small disks. These disks were weighed to the nearest centigram, placed in beakers containing acid solutions of varying concentrations, and allowed to remain for a constant period of time. They were then removed, drained, and reweighed. The increase in weight due to imbibition of water was calculated to the amount imbibed per gram of moist gluten. The experiments were then repeated, except that a series of salts was added to the different concentrations of the acids. The addition of the salts caused a diminution of the water imbibition. They found that in dilute acids the gluten swells and, "the disks puff up and take on an appearance somewhat resembling cotton balls, finally becoming transparent, soft, and gelatinous."

***Wood allowed the gluten to imbibe water until it lost coherence and began to disperse as a sol. Upson and Calvin, on the other hand, determined the weight of the water imbibed by the gluten in a fixed period of time and before imbibition had progressed far enough to cause dispersion.**

They furthermore found that the taking up and giving off of water was largely reversible and, by neutralizing the acid after swelling of the disks had taken place, it would lose water and again become a firm coagulum.

In a later publication, Upson and Calvin (**1916**) give results of further studies on the colloidal swelling of wheat gluten as related to baking strength of flour and conclude that, "Strength is related to soluble acid and salt content of the flour. Flours containing acids and salts in such combinations as to favor water absorption will behave as 'weak' flours, whereas those containing acids and salts in such combinations as inhibit water absorption will behave as strong flours when baked."

It should be noted that this finding is in many respects similar to that of Wood.

At about the same time Mohs (**1915**) discussed gluten formation and the value of wheat flour from the standpoint of colloid chemistry. His conclusions, arrived at largely from theoretical considerations, are that the hydrophilic colloids, gliadin and glutenin, form an unelastic gel with a honeycomb-like structure, and that gluten formation depends upon the mutual irreversible adsorption of the gluten proteins. Mohs regards gliadin as the most important component of the gluten and states that it functions as a protective colloid. He regards quality of gluten as depending upon the degree of hydration and believes that dehydration of the gluten gel is not reversible and that influences which lead to dehydration make a permanent impress upon the colloidal behavior of the gluten. He points out the influence of organic acids in increasing hydration and of neutral salts in dehydrating the gluten. In a later paper Mohs (**1922**) has extended his argument in regard to the colloidal phenomenon exhibited by the wheat protein. Here again the argument is based upon analogy and theoretical considerations rather than upon experiments which he has himself carried out. We can accordingly dismiss his views as lacking experimental proof, although in the main they appear to be in agreement with those of Wood, Wood and Hardy, Upson and Calvin, Ostwald, Lüers, and Lüers and Ostwald.

Ostwald (**1919**) has likewise discussed the problems of bread manufacture from the standpoint of colloid chemistry, pointing out that, whereas we have many researches upon the purely chemical phases and the fermentation and enzyme problems which are involved, the physico-chemical and colloidal phenomena have been largely neglected.

Lüers and Ostwald (**1919**) studied the viscosity of flour pastes, using an Ostwald viscosimeter. The flour pastes were prepared by pouring a suspension of flour-in-water into boiling water, thus gelatinizing the starch. They believe that there are two major problems in bread manufacture which should be studied from the standpoint of viscosity. The one has to do with dough formation and the other deals with dough baking. These authors believe that the properties making for a good dough and those making for good baking conditions are distinct.

In an investigation of the different grades of flour they found that the viscosities of flour pastes divided themselves into three classes; the patent flours showed a greater viscosity than did the straight flours, while the clear flours showed the least viscosity. This was found to be true for both wheat and rye flours. They concluded that the viscosity of flour pastes was directly proportional to the starch content and suggested that the measurement of the viscosity of flour pastes be used as a method for the determination of the starch content of flours. The addition of various amounts of sulfuric acid was found to have little effect on the viscosity of flour pastes.

Suspensions of flour-in-water without heating were investigated, the flour

concentrations ranging from 7 to 20 per cent. It was found that rye flours of the same grade and concentration gave relatively much more viscous solutions than did wheat flours, and the authors suggested this as a method of differentiating between the two. In the case of the wheat flour suspension, the lower the grade of the flour, the more viscous was the solution. This is just the reverse of the behavior of the flour pastes prepared by heating the flour-in-water suspension so as to gelatinize the starch. Lactic acid was found to markedly increase the viscosity of (unheated) wheat flour suspensions, the effect being more pronounced, the higher the grade of the flour. Lactic acid seemed to have no effect in increasing the viscosity of rye flour suspensions.

Lüers (**1919**) studied the effects of acids, bases, and salts on solutions of gliadin prepared from wheat and rye flours. With acids the maximum viscosity was attained at 0.0004 to 0.00066 N hydrochloric acid, with 0.0022 N sulfuric acid, and with 0.018 to 0.0011 N lactic acid. With alkali the maximum viscosity was reached at 0.0022 N sodium hydroxide, and at 0.013 to 0.014 N barium hydroxide. Hydrochloric acid was found to increase the viscosity of gliadin dissolved in alcohol. In all of the experiments reported, no essential difference was noted between the gliadin from wheat and that from rye, and the author concluded that they are identical. This confirms the earlier conclusions of Gróh and Friedl (**1914**).

Lüers and Ostwald (**1920**) studied the viscosity of suspensions of two poor rye flours and found that both gave low viscosity values, one having only about one-fourth the viscosity of normal rye flour of the same grade. They emphasized that the best flour would probably show an optimum viscosity, neither too high nor too low.

Lüers and Ostwald (**1920a**) discuss the work of Upson and Calvin (**1915, 1916**) on the colloidal swelling of wheat gluten and state that their own conclusions are in essential agreement. While both emphasize that it is the quality and not the quantity of the gluten which is important, nevertheless they seem to believe that the quality of the gluten is regulated by the acids and salts present in the flour or added to it in the bread-making process.

Prior to this work Gortner and Doherty (**1918**) undertook a study of certain colloidal properties of the glutens from strong and weak flours. The method employed was the Hofmeister method as used by Upson and Calvin, and consisted in following changes in hydration of gluten disks when immersed in solutions of various acids and salts. The only difference in technic employed by Gortner and Doherty over that employed by other workers is that glutens from both strong and weak flours were used in the experiments, whereas Wood and Hardy, Upson and Calvin, and Lüers and Ostwald, all made experiments upon one type of gluten and reasoned by analogy from such experiments as to the factors which were involved in the strong and weak flour problem. Gortner and Doherty pointed out that, while in many instances it is possible to reach valid conclusions by reasoning from analogy, it is a rather dangerous procedure when the material in question is a lyophilic gel.

Gortner and Doherty conclude that the findings of Wood and Hardy, and of Upson and Calvin, that "the variations in coherence, elasticity, and water content observed in gluten extracted from different flours, are due rather to varying concentrations of acid and soluble salts in the natural surroundings of the gluten than to any intrinsic difference in the glutens themselves" do not hold when both types of gluten are investigated. On the contrary, they conclude:

(1) "Although the moist glutens from these flours differ widely in 'quality' and in physical properties, they are hydrated to almost exactly the same extent.

(2) "Gluten from a weak flour has a much lower rate of hydration than gluten from a strong flour.

(3) "Gluten from a weak flour has a much lower maximum hydration capacity than gluten from a strong flour, changing from a gel to a sol at a much lower degree of hydration.

(4) "There is an inherent difference in the glutens from the strong and weak flours. The physico-chemical properties of the glutens from the different flours are not identical and would not be identical even if the flours had originally had the same acid and salt content.

(5) "The difference between a strong and weak gluten is apparently that between a nearly perfect colloidal gel with highly pronounced physico-chemical properties, such as pertain to emulsoids, and that of a colloidal gel in which these properties are much less marked." *

Sharp and Gortner (**1922**) later repeated the work of Gortner and Doherty on a new series of flours and reached identical conclusions. They also showed that upon drying the glutens from strong and weak flours the properties of the glutens became more nearly alike. This observation is in complete accord with the theory that the strong gluten is strong because of more pronounced colloidal properties, inasmuch as it is well known that alternate wetting and drying of a colloidal gel breaks down the gel structure.

In more recent papers, Gortner and Sharp (**1923**, **1923a**), Sharp and Gortner (**1923**, **1923a**), and Sharp, Gortner, and Johnson (**1923**) have made a rather detailed study of some of the colloidal properties of wheat flour as related to flour strength. They have again reached the conclusion that *gluten quality is determined primarily by the colloidal condition of the gluten gel.*

Hydration changes in the gluten colloids were followed by observing changes in viscosity, using a MacMichael viscosimeter. It was found that this method was much more accurate and less laborious than was the old method of weighing gluten disks, and in addition could be applied to the entire flour sample as contrasted with washed-out samples of gluten. Figure 2 shows typical experiments.

A study of hydrogen ion concentration in relation to maximum hydration showed that a maximum imbibition in acids occurs at approximately a pH of 3.0 (cf. Fig. 3 where the data in Fig. 2 are redrawn in terms of pH) and in alkalies at approximately a pH of 11.0. The presence of the natural salts in the flour or salts added to the flour-water suspension depress imbibition but do not shift the hydrogen ion concentration at which maximum imbibition takes place. The conclusion that the proteins of a weak flour have a slower rate of hydration and a lower maximum imbibition capacity was confirmed.

A study of the proteins present in the flours showed that the physico-chemical properties of the gliadins from both strong and weak flours are identical but that the colloidal properties of the glutenins may be widely different.

Woodman (**1922**) investigated certain of the physico-chemical properties of the proteins isolated from strong (Canadian) flours and weak (English) flours, using certain physico-chemical methods originated by Dakin. Dakin (**1912**) has shown that the optical rotations of proteins are markedly altered by treatment with dilute alkali. Dakin explains this behavior as an enolization at the peptide linkage. Woodman (**1922**) followed the change in optical rotation of gliadin and glutenin from his strong and weak flours when race-

* Cumulative protective action in mixtures is a factor that demands consideration. *See, e.g.*, J. Alexander, in Vol. I of this series, p. 826, where reference is made to the gluten in flour, among other things. Apart from chemical and physical differences, relatively small variations in percentage composition with the same constituents, or the presence of small amounts of impurities, may produce differences in practical working properties quite out of proportion to what might be expected. Many mixtures like alloys and glasses exhibit phenomena of this type, which are not always calculable or easily comprehensible. *See also* paper on Internal Medicine by H. Schade in Vol. II of this series, which considers the swelling of protein mixtures. J. A.

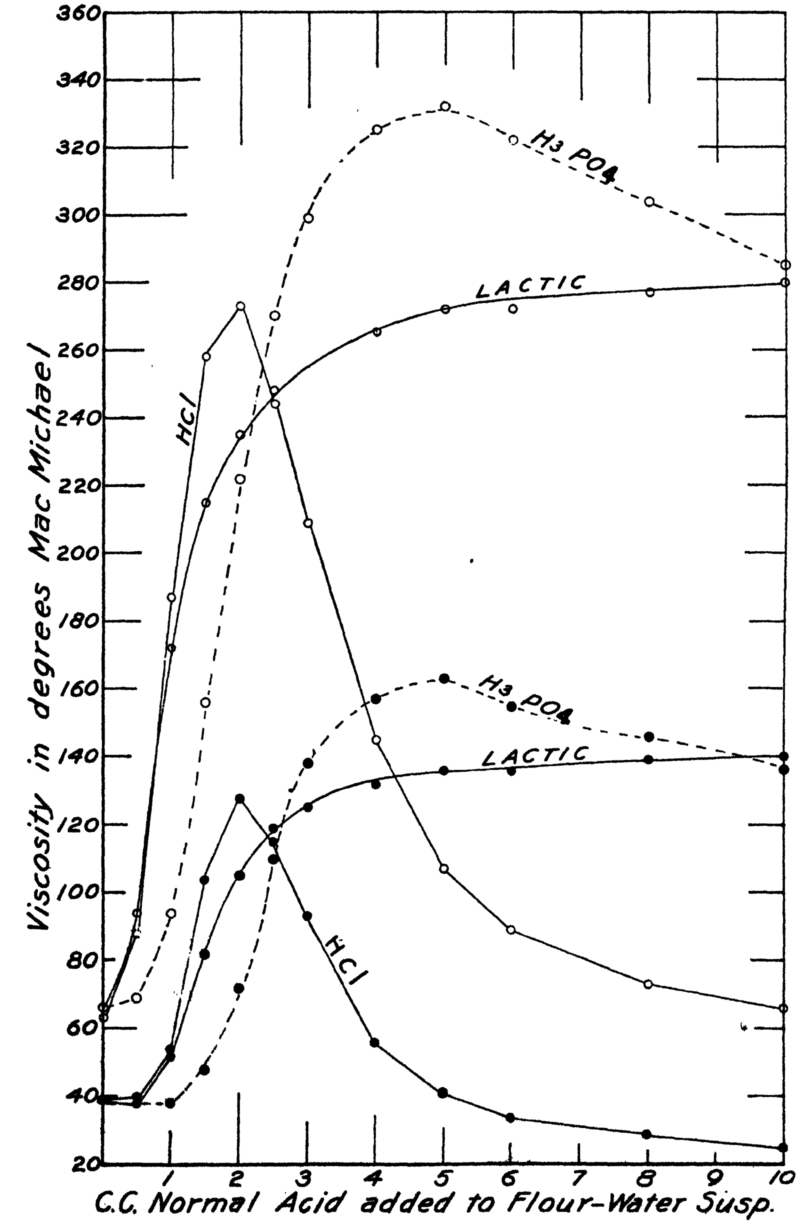

FIG. 2.—Imbibition curves of wheat flour proteins as influenced by the various acids. The open circles are a strong flour, the solid dots a weak flour (after Gortner and Sharp).

mized with alkali at 37° C. and found that the gliadin from the two sources was identical. On the other hand, the glutenins showed different racemization phenomena. Thus, Woodman concluded that the difference between a strong and a weak flour is dependent upon the glutenin fraction, the same conclusion

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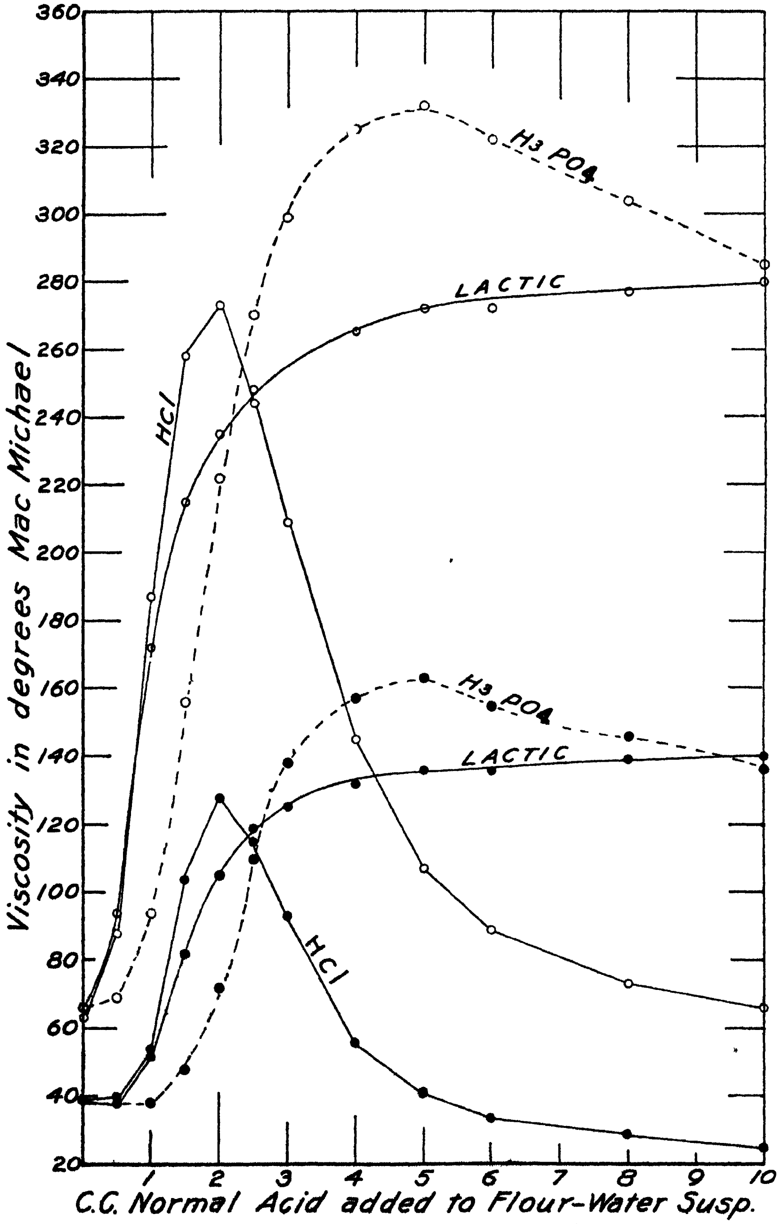

FIG. 2.—Imbibition curves of wheat flour proteins as influenced by the various acids. The open circles are a strong flour, the solid dots a weak flour (after Gortner and Sharp).

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that Sharp and Gortner (1923) reached using entirely different methods. However, Woodman's findings dealt with the chemical nature of glutenin rather than its colloidal behavior. Woodman's experiments have been repeated by

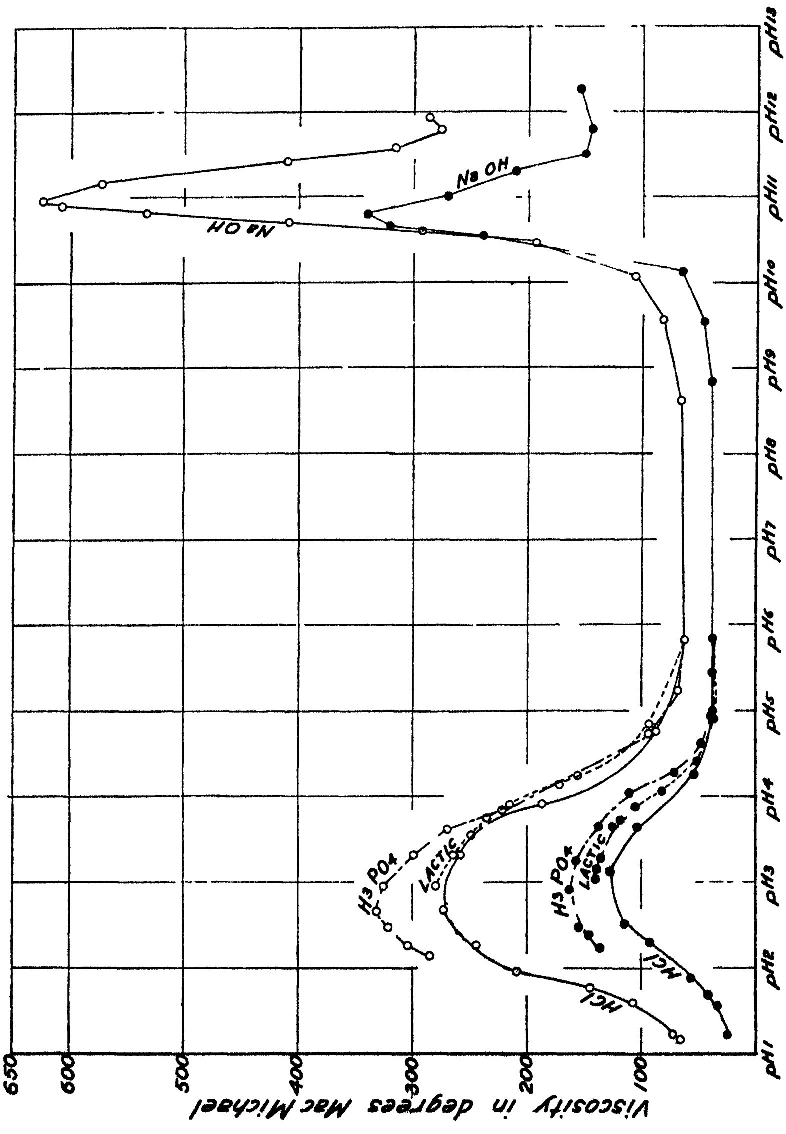

Fig. 3.—Imbibition curves of wheat flour proteins as influenced by hydrogen ion concentration. The open circles are a strong flour, the solid dots a weak flour (after Gortner and Sharp).

Blish and Pinckney (1924), and they have not been confirmed. These authors conclude,

"It is highly improbable that variations in the respective flour strengths of our commercially important wheats can ever be attributed to differences in the chemical configurations of their respective glutenin molecules. This is in disagreement with the conclusions of Woodman (1922).

"Differences in physical or colloidal properties of glutens appear to be due either to different states of molecular aggregation or to influences of electrolytes or other agents at present unknown."

Having become convinced that flour strength (insofar as gluten quality is concerned) was a colloidal phenomenon, Sharp and Gortner (**1923a**) investigated the relation between the maximum viscosity obtainable with lactic acid and the flour concentration, the protein concentration, and the glutenin concentration in the mixtures which were used for the viscosity determinations, in the hope of finding a constant which could be used to denote gluten "quality." Figure 4 shows typical experiments. They found that the equation,

$$\log \text{viscosity} = \log a + b \log \text{concentration},$$

held for either flour, protein, or glutenin concentration. The significant constant in this equation appeared to be b which is the tangent of the angle made by the logarithmic curve with the axis of abscissa (Gortner, **1924**). The constant a is the logarithm of the viscosity reading, when the logarithmic curve is extrapolated to unit concentration. It may be added that the above equation is the logarithmic expression for the Freundlich adsorption isotherm.

Hendel and Bailey (**1924**), in the study of the viscosity of leached and acidulated flour-water suspensions from a series of mill streams from the same wheat, found considerable variation in the Sharp and Gortner quality constant b, which would seem to indicate that the colloidal properties of the proteins in the various mill streams were not identical, certain mill streams being more desirable for bread-making purposes than others. This fact had long been known, but it is of interest to note that the viscosity relations were in the same direction as might have been anticipated.

Johnson and Bailey (**1924**) studied the viscosity of leached flour-in-water suspensions for a series of cracker flours, using the method of Sharp and Gortner, and reported a high quality constant b for these flours.

Blish and Sandstedt (**1925**) were the first to report data casting doubt upon the value of the constant b as indicating gluten quality. They studied the correlation between the quality constant b of the Sharp and Gortner equation and the loaf volume of a series of Nebraska wheat flours and found no appreciable correlation, although they do remark that there is some correlation between the viscosity of a single unleached flour-in-water suspension and the loaf volume of the bread.

Vogel and Bailey (**1927**), in a study of durum wheats, found that the viscosity of the leached and acidulated suspensions of durum wheat flours are very much lower than similar preparations from the bread wheats and note that this method could be used to distinguish between the two types of flour. They report, however, that the constant b of the Sharp and Gortner equation for durum wheats falls within the range previously reported for the bread wheats and confirm the doubts of Blish and Sandstedt as to its value as indicating gluten quality.

Somewhat similar results were obtained by Grewe and Bailey (**1927**) who report the viscosity of leached and acidulated suspensions of seventeen wheat flours and the calculated constant b of the Sharp and Gortner equation. They found no relation between this constant and the loaf volume, and when the data were subjected to statistical analysis, the correlation coefficient, $r = +0.074 \pm 0.163$, was less than the probable error.

About this time Johnson (**1927**) began a rather extensive study of factors influencing the viscosity of flour-water suspensions, with particular reference

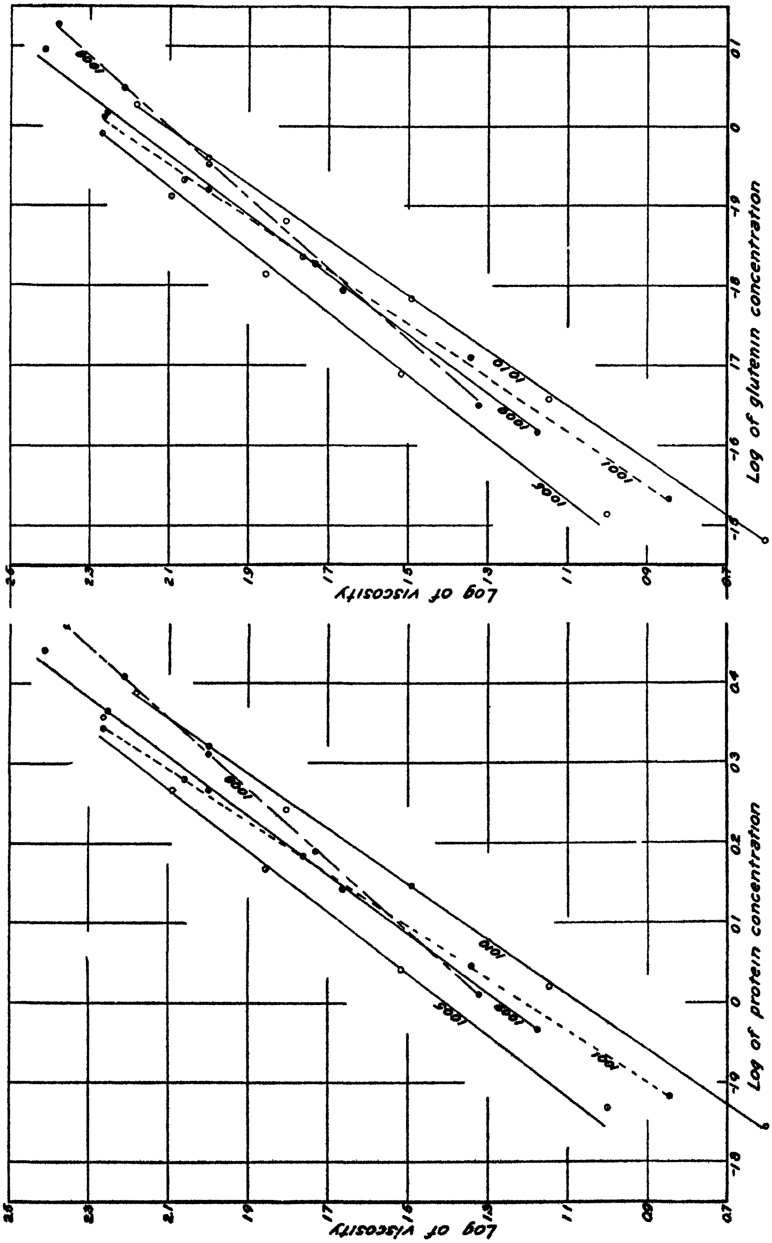

FIG. 4.—The relation between the maximum viscosity obtainable with lactic acid, and the protein and glutenin concentration, for a series of flours of varying strength (after Sharp and Gortner).

to the effects of temperature, degree of hydration, and hysteresis due to methods of manipulation. He found that the constant b of the Sharp and Gortner equation is a constant for any given sample of flour at temperatures ranging from 15° to 40° C., but that there is a sharp change in the value of this constant at temperatures higher than 40° C., constant b progressively increas-

ing up to the maximum temperature which he studied, 80° C. He found that constant *a* of the Sharp and Gortner equation varies from temperature to temperature, and, as a general rule, tends to increase with increasing temperature. He emphasized in particular that any variation in the temperature of the flour-water suspension during the preliminary preparation of the suspension would be reflected in an alteration of the constant *a* of the equation, and that in order to obtain constant and duplicatable viscosity readings, one must subject all of the samples of flour to a very rigidly controlled and predetermined technic. Johnson noted that the degree of hydration of the flour colloids is markedly increased by an increase in temperature and that the degree of hydration increases sharply at approximately 50° C. It seems probable that this sharp change at 50° C. may be attributed to the starch portion of the flour, as contrasted with the protein portion, the protein apparently contributing the greatest viscosity effects at the lower temperatures.

In a continuation of this study Johnson and Herrington (**1928**) studied the factors involved in the estimation of viscosity of flour-water suspensions, with particular reference to the effect of hydrogen ion concentration during the extraction or digestion period. They note that maximum viscosities were obtained with acidulated flour-water suspensions where extractions or digestions were carried out at a hydrogen ion concentration equivalent to approximately pH 5.0 and that those suspensions which exhibited the highest viscosity on acidulation had been previously leached with water, so that approximately 50 per cent of the nitrogen in the original flour had been removed by decantation. They emphasize the importance of controlling the hydrogen-ion concentration of the leach water when using the Sharp and Gortner technic; otherwise it is difficult to obtain results which can be readily duplicated. (Variation in other ions than the H-ion might also be material. J. A.)

In a third paper Johnson and Herrington (**1928a**) considered the effect of carbon dioxide in the waters used for extraction and note that if the water which is used for extraction contains carbon dioxide, the viscosities of the final acidulated flour-water suspensions will be somewhat higher than if carbon-dioxide-free water had been used, the difference in viscosity being increased somewhat in proportion to the amount of water which was used for extraction. The water containing carbon dioxide did not remove greater quantities of electrolytes than did neutral water, and the increased viscosity did not appear to be due to the difference in hydrogen ion concentration of the different waters. The water containing carbon dioxide removes somewhat larger amounts of protein, and they suggest that in all probability certain of the proteins of wheat flour operate to depress the viscosity of acidulated leached flour-water suspensions and that when these proteins are removed by leaching, higher viscosities are obtained.

As a further extension of the viscosity study, Johnson, Herrington, and Scott (**1929**) have applied the viscometric method to the measurement of the proteoclastic activity of wheat flour. This had previously been done by Collatz (**1922**), Sharp and Elmer (**1924**), Cairns and Bailey (**1928**), and Kent-Jones (**1927**). Johnson *et al.* again emphasize the necessity of adhering to a rigid, predetermined technic if comparable results are to be secured. They note that since flour strength appears to reside in the glutenin fraction and since the glutenin fraction is the fraction which affects the viscosity of acidulated and leached flour-water suspensions, a decrease in viscosity means that the glutenin fraction has been attacked by the proteolytic enzymes, and accordingly the measurement gives an insight into changes in that protein fraction which contributes the most to the desirable colloidal properties of the flour.

Blair, Watts, and Denham (**1927**), in a study of the viscosity of flour-water suspensions, suggest that the equation,

$$\log \text{viscosity} = \log a + b \text{ concentration},$$

has a greater practical utility than the expression of the Sharp and Gortner equation, i.e., instead of plotting the logarithm of viscosity against the logarithm of concentration, they suggest that the logarithm of viscosity be plotted against the numerical concentration.

Denham, Blair, and Watts (**1927**) report the Ostwald type of viscosimeter as satisfactory for measurements on flour-water suspensions up to a 30 per cent flour concentration. They confirm the earlier observations of Sharp and Gortner that the viscosity of a flour-water suspension decreases with time and suggest that this decrease may be due to syneresis. They believe that this "fall back" in viscosity may be, to some extent, correlated with the strength of the flour and again emphasize the necessity of following a rigidly prescribed technic in making viscosity studies on lyophilic systems.

Van der Lee (**1928**) objects to the equations which have been proposed by Sharp and Gortner, and Blair, Watts, and Denham, and discusses viscosity of flour suspensions with particular reference to Einstein's (**1906, 1911**) formula for the viscosity of colloid systems.

$$\eta' = \eta\ (1 + K\phi)$$

where η' = viscosity of the colloidal system, η = viscosity of the pure solvent, and ϕ = the relation between the volume of the suspended particles and the total volume of the system, with K, a constant which for spherical particles approximates a value of 2.5. He notes that the Sharp and Gortner equation does not conform to the requirements of the Einstein equation and that consequently the Sharp and Gortner equation should be considered as an empirical equation and their method for studying viscosity as an arbitrary method. It may perhaps be of interest to note that the equation proposed by Kunitz (**1926**),

$$\eta = \frac{1 + 0.5\,\phi}{(1 - \phi)^4}$$

where η = the observed viscosity, and ϕ has the same meaning as in the Einstein equation, may be more accurate. The great difficulty in applying either of these equations to lyophilic systems lies in establishing a true value for ϕ.

Whether or not any one of the constants of a viscosity equation will yield a "quality constant" appears doubtful in the light of the diverse views which have been presented. Certain mill laboratories, however, have adopted viscosity measurements as a part of their routine testing technic. Thus, Morgan (**1924**) reports that viscosity measurements of an acidulated but unleached flour-water suspension are of great value in the mill laboratory, both in determining gluten quality and in controlling blends of wheat so as to produce a flour of uniform baking properties; and Smith (**1925**) likewise states that viscosity measurements made on unleached, acidulated flour-water suspensions at a single flour concentration yield data which are of value in determining the gluten quality. His experience is that all flours showing a high viscosity have excellent baking properties, and flours which show low viscosity, in general, have inferior baking properties, although there are some flours of low viscosity which yield excellent loaf volumes.

In the foregoing discussion no distinction was made by the various workers between true viscosity and plasticity. Sharp (**1926**) undertook a study to de-

termine whether or not flour-in-water suspensions are truly viscous or whether they are in reality plastic, and reports that suspensions containing 9 per cent or more by weight of flour on the dry basis are plastic rather than viscous. Accordingly, their properties may be expressed by both the terms, "consistency" and "yield value."

Dunn (1926) confirmed the observation of Sharp that wheat-flour-in-water suspensions are plastic when the concentration of wheat flour approximates 9 to 10 per cent by weight, and further notes that there is a marked variation from flour to flour in the consistency and yield value as determined by plasticity measurements. However, plasticity studies have not as yet provided a gluten quality constant.

St. John (1929), in a study of the plasticity of a series of flour-water suspensions, demonstrated that hysteresis occurs, in that the suspensions increase in mobility as the suspension ages. No correlation was found between the mobility of the flour-water suspensions at constant protein concentration and the volume of the resulting loaf. The yield value of all of the flours at constant concentration was essentially the same.

St. John and Bailey (1929) report upon the plasticity of doughs and of flour-water suspensions to which dry skim milk had been added, using a modified Bingham and Murray (1923) plastometer. They have likewise studied these systems by use of the Chopin extensimeter (*vide infra*) and with a new and rather novel technic in which a micro watt-hour meter was attached to an experimental dough-mixing machine, so that the power required to operate the dough-mixing machine for a definite number of revolutions could be accurately ascertained. The wattage required for the operation of the empty unit, or the power requirement of the motor, gears, and the mixing machine containing no dough, was first observed. This value was then subtracted from the wattage of the unit with dough in the mixing machine, and the difference recorded as the power necessary to move the blades of the mixing machine a definite number of revolutions through the dough mass. Remarkably constant and duplicatable results were obtained by use of this apparatus, and it is believed such technic can be used to advantage in studying the relative plasticity of extremely dense plastic systems and in studying changes in the plasticity of such systems with time or with the addition of other ingredients to the mass. A somewhat similar arrangement has apparently been used in the rubber industry as evidenced by the "power chart" presented by Trumbull (1928).

Chopin (1921) has attacked the colloidal properties of the dough mass in a somewhat different manner. He devised a unique apparatus for measuring the elasticity, and possibly to some extent the plasticity of a dough mass. In this apparatus a disk of dough 3 mm. thick is clamped in place and air is forced underneath this dough disk, raising and stretching the dough membrane in the form of a hemispherical bubble. The volume which can be formed from a given mass of dough and the pressure at which the bubble ruptures and the membrane collapses is taken as a measure of elasticity or extensibility. Chopin suggests that extensibility in his apparatus can be correlated with loaf volume by use of the formula,

$$V - V_0 = K\sqrt{e},$$

where V = the final specific volume of the baked loaf, V_0 = the specific initial volume of the unfermenting dough, e = the coefficient of extension of the dough which is numerically equal to the surface of the dough membrane at the instant of rupture, and K = a constant. In a later paper, Chopin (1927)

attaches an automatic pressure recorder to the apparatus and traces in terms of surface area and gas pressure, the curve of extensibility to the point of rupture, calculating the specific energy of deformation in ergs per gram of flour, and suggests that the apparatus may be used for blending wheats of various origin in order to produce flours of uniform quality for the trade.

Bailey and Le Vesconte (**1924**) studied the extensibility of the doughs prepared from a series of wheat flours, using the Chopin extensimeter. They note that prolonged mechanical treatment or mixing of the dough decreases the extensibility, probably due to the breaking down of the gel structure. The extensibility of the dough depends to a large degree upon the amount of water which is added in the dough batch, rising to a maximum at an optimum absorption content and then falling off rapidly as more water is added. The dough was found to show its greatest extensibility at approximately a pH of 6.0. Below a pH of 5.0 and above a pH of 7.0 the elasticity of the dough was greatly reduced. They conclude that the Chopin extensimeter is capable of affording a useful index of many of the colloidal properties of the flour under bake shop conditions.

Johnson and Bailey (**1924**), using the Chopin extensimeter in a study of fermenting cracker doughs, found that the extensibility of the dough increased with the fermentation period for about three hours, following which there was a very rapid decrease in the extensibility of the dough until at the eighteen-hour stage the extensibility was essentially zero. At least a part of this change appeared to be due to the increasing hydrogen-ion concentration of the dough as fermentation progressed, thus bringing about a more or less complete dispersion of the gluten proteins, and if the hydrogen-ion concentration was reduced at the end of the fermentation period by the addition of sodium bicarbonate, a considerable recovery of extensibility occurred. They showed in further studies involving viscosity measurements that the elasticity, the tenacity, and the viscosity of the dough gel are all decreased by prolonged fermentation. Later Grewe and Bailey (**1927**) studied seventeen flours, using the Chopin extensimeter, and while the parallelism between loaf volume and extensibility was not exact, nevertheless they found a correlation coefficient of $r = +0.671 \pm 0.076$ between these two variables.

Engledow (**1928**) has devised a modified apparatus based somewhat on the principle of the Chopin extensimeter, in which air pressure is applied to one side of a thin sheet of dough distending it into a bubble, the pressure being progressively increased until the dough bubble bursts. He notes that if two doughs are compared side by side, the dough which bursts first is of the lower baking strength.

Harrel (**1927**) suggests the use of a penetrometer for determining the stiffness of doughs as they come from the mixing machine and suggests technic whereby the penetrometer can be used to determine the optimum amount of water which should be added to the flour in the dough formula.

Kress (**1924**) suggests an apparatus to measure the physical properties of the washed gluten, the apparatus consisting of a device whereby a sheet of the washed gluten is clamped between two parallel plates having a three-fourths inch hole in the center of each, and the gluten disk so formed subjected to the downward pressure of a spherical plunger one-half inch in diameter. Force is applied to the plunger, and the curve of gluten extensibility up to the point of rupture is traced by a recording pen on a chart. He believes that the results so obtained give a more or less accurate measure of gluten quality, the more elastic and tenacious glutens having the high baking strength, and adds that the measurements agree with subsequent loaf volumes.

Wheat Flour Proteins and the Lyotropic Series.

It has already been noted that Osborne characterized five proteins as present in wheat flour, an albumin, a globulin, a prolamine, a glutelin, and a proteose. Inasmuch as no single sample of wheat flour had been studied with respect to all five of these proteins, Hoffman and Gortner (**1927**) undertook such a study. To their surprise they found that extraction of the wheat flour with 5 per cent potassium sulfate did not yield protein fractions similar to those which were obtained by extracting with 10 per cent sodium chloride solution. They, therefore, raised the question as to the definition of the term, "globulin," and as to the nature of the process which was involved in the extraction of the "salt-soluble" proteins and as to the extent of the effect of various anions and cations on protein "solubility." The Physiological and Biochemical Committees on Protein Nomenclature (**1908**) defined globulins as "simple proteins insoluble in pure water but soluble in neutral solutions of salts of strong bases with strong acids (the precipitation limits with ammonium sulfate should not be made a basis for distinguishing the albumins from the globulins)." It would appear that this definition is not exact, in that no statement is made as to the concentration of the salt solution. In most textbooks this definition is given somewhat as follows: "Simple proteins, heat-coagulable, insoluble in water, but soluble in dilute solutions of the salts of strong bases with strong acids." Even here there may well be a difference of opinion as to what constitutes a "dilute solution," and it would appear from the definition that all salts of strong acids with strong bases should be equally effective in "dissolving" globulins.

Gortner, Hoffman, and Sinclair (**1928, 1928a, 1929**) accordingly undertook an investigation of the effect of various salt solutions upon "protein solubility," using twenty-one different salts, most of them in four different concentrations, and using twelve different wheat flours as the biological material which was investigated.

Table 1 shows certain of the characteristics of the wheat flours which were used and lists the types of wheat from which the flours were milled, the commercial millers' grade, the ash content, the crude protein content ($N \times 5.7$), and the volumes of the resulting loaves of bread. These same flours had been earlier used by Grewe and Bailey (**1927, 1927a**) in certain cereal chemical studies. Table 2 lists the various percentages of the total protein which were extracted from each flour by the various salt solutions in 1.0 *N* concentration or by a single salt solution of 1.0 *N* concentration from the various flours, and also lists the average per cent of protein extracted by the different salts from a single flour and the average per cent for the different flours extracted by a single salt solution, as well as giving the maximum and minimum ranges of the protein extracted from the various flours.

Figure 5 is a graphic representation of the average percentage of protein extracted from the 12 wheat flours by the various concentrations of the salt solutions which were used.

Viewing these data from the standpoint of colloid chemistry, it is evident that protein "solubility" is not solubility in the sense in which that term is used in physical chemistry, but that we are here dealing with peptization and that the various salts do not peptize wheat flour proteins to the same degree. There is a pronounced lyotropic or Hofmeister series of anions, ranging themselves in the order of increasing peptizing effect of $F < SO_4 < Cl < \text{tartarate} < Br < I$, and there is a less pronounced but still distinct lyotropic series of cations in the order of increasing peptization of $Na < K < Li < Ba$

< Sr < Mg < Ca. The lyotropic effects appear to be due to the specific properties of the anion and cation of the salt and were observable and measurable at a constant hydrogen-ion concentration. The alkali halides cause decreasing peptization with increasing salt concentration, whereas the halides of the alkaline earths, as a rule, showed an increased peptization with an increasing salt concentration. Since the data showed that 1.0 *N* solutions of KF extracted an average of 13 per cent of protein, KCl 23 per cent, KBr 37

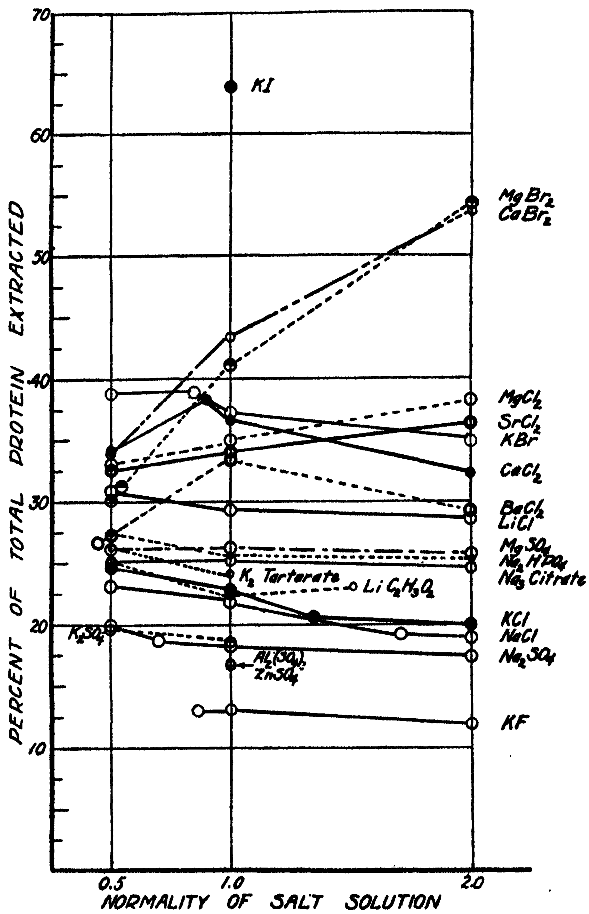

FIG. 5.—Average percentage of protein extracted from 12 wheat flours by various concentrations of salt solutions (after Gortner, Hoffman, and Sinclair).

per cent, and KI 64 per cent from the wheat flours, the question was raised as to which salt extracts the globulins. It was suggested that the generally accepted definition of globulin was so ambiguous as to be essentially meaningless.

Prior to these studies it had been generally assumed that the "gluten" proteins of a wheat flour could be estimated by subtracting from the total protein that fraction of the protein which was "soluble" in dilute salt solution. The studies of Gortner, Hoffman, and Sinclair, however, demonstrated that

TABLE 1. *Protein Content (Dry Basis) and Loaf Volume of the Flours Used.**

Lab. No.	Type of Wheat	Grade of Flour	Crude Protein Per Cent	Ash Per Cent	Loaf Volume cc.
1	Club and soft white	Straight	9.73	0.62	1810
2	Canadian hard spring	55% Patent	13.99	0.51	1990
3	Hard spring	80% Patent	13.07	0.48	2180
4	Hard winter	80% Patent	12.53	0.45	2130
5	Canadian hard spring	50% Patent	14.29	0.47	2170
6	Turkey red and hard red winter	82% Patent	12.34	0.51	2140
7	Soft winter	48% Patent	10.61	0.43	1990
8	Soft winter	Short Patent	10.63	0.51	1970
13	Red winter	95% Patent	10.09	0.46	2020
14	Blend hard winter and hard spring	Patent	12.76	0.52	2150
15	Soft red winter	40% Patent	12.49	0.42	2200
17	Durum	Straight	13.64	0.86	1940

* Data of Greve and Bailey (1927).

the nitrogen which was extracted by a salt solution from any given flour did not necessarily indicate the proportion of the non-gluten proteins present in that flour. In other words, certain of the salts appear to peptize either the gliadin or the glutenin. More recent work (Sinclair, 1929) has shown that a large portion of the gliadin is rather readily peptized by certain of the salt solutions, and Staker and Gortner (1931) have demonstrated that the findings of Gortner, Hoffman, and Sinclair on wheat flours are applicable to seed meals in general.

Inasmuch as Gortner, Hoffman, and Sinclair demonstrated that the various flours showed a marked difference in the degree to which their proteins were peptized by individual salt solutions, it became of interest to ascertain whether or not the ease with which the flour proteins were peptized could in any way be related to flour strength. Gortner (1927) accordingly determined certain of the correlation coefficients (r_{xy}) between the percentage of protein peptized by a given salt solution and the loaf volume of the bread which could be baked from that particular flour, using the correlation formula suggested by Harris (1910).

$$r_{xy} = \frac{\frac{\Sigma xy}{N} - \overline{xy}}{\left[\sqrt{\frac{\Sigma(x)^2}{N} - (\bar{x})^2}\right]\left[\sqrt{\frac{\Sigma(y)^2}{N} - (\bar{y})^2}\right]}$$

$$Er = \pm\frac{0.6745(1 - r^2)}{\sqrt{N}}$$

where Σ = the sum of the numbers involved, x = loaf volume, y = per cent of protein extracted by the salt solution, $\bar{x}$ and $\bar{y}$ = the mean values for x and y for the entire series of determinations, N = number of samples involved, and Er = the probable error.

Table 3 shows the coefficients of correlation which were obtained. It will be noted that, with the exception of the average for the 2.0 *N* solutions, there is a very high negative correlation in all instances. The exact reason for the reversal of signs and lower correlation in the 2.0 *N* series can only be ascertained by calculating the coefficients for the individual salts. This has not been done. Probably the reversal of signs is caused by the change in the per cent of protein extracted by the salts of the alkali metals, in which solutions the peptization is depressed, and the salts of the alkaline earths where, in general,

TABLE 2. *Percentage of Total Protein Extracted from Wheat Flours by 1.0 Normal Salt Solutions*

Salt	Flour No.												Range of flours	Average of flours
	1	2	3	4	5	6	7	8	13	14	15	17		
Li Acetate	29.4	19.3	19.0	16.9	19.4	21.4	23.7	26.0	29.1	21.6	20.2	21.9	16.9–29.4	22.32
LiCl	39.3	26.8	27.5	23.9	27.0	29.1	29.9	30.3	34.0	28.1	26.3	29.7	23.9–39.3	29.32
NaCl	25.4	21.2	20.2	19.2	18.3	21.2	22.2	23.7	26.8	21.6	17.9	22.5	17.9–25.4	21.68
Na_2SO_4	25.7	16.5	16.0	14.8	15.6	17.2	18.1	18.9	22.9	18.7	14.8	18.8	14.8–25.7	18.20
Na_3 Citrate	42.5	lost	17.3	15.6	18.2	20.7	29.5	31.2	34.1	22.7	23.8	20.8	15.6–42.5	25.13
Na_2HPO_4	41.5	22.1	19.4	16.6	19.4	21.6	29.9	31.4	36.5	23.3	24.0	21.8	16.6–37.5	25.62
KF	18.0	11.9	11.2	10.5	11.4	12.6	12.4	14.3	15.5	13.0	10.8	15.2	10.5–18.0	13.07
KCl	30.4	21.7	20.7	18.7	20.9	22.0	22.3	25.0	27.7	22.7	17.9	23.3	18.7–30.4	22.77
KBr	48.6	39.4	35.7	30.1	36.3	35.5	36.3	38.3	41.2	35.0	31.8	38.4	30.1–48.6	37.22
KI	73.9	69.5	60.5	55.4	64.2	66.1	61.6	63.1	68.0	63.6	56.5	64.3	55.4–73.9	63.89
K_2SO_4	26.2	16.4	16.1	14.8	15.8	17.2	18.9	20.2	23.3	19.9	14.8	19.5	14.8–26.2	18.59
K_2 Tartrate	34.6	21.7	21.7	18.4	20.2	22.3	28.7	28.1	25.0	24.1	23.6	21.1	18.4–34.6	24.12
$MgCl_2$	47.0	34.3	33.1	29.1	31.4	33.6	34.8	36.5	40.2	33.0	30.9	36.0	29.1–47.0	34.99
$MgBr_2$	46.5	40.9	38.4	32.9	38.9	38.2	42.7	42.5	46.4	37.5	37.2	39.2	32.9–46.5	40.11
$MgSO_4$	41.6	26.6	22.0	19.6	21.3	23.9	27.3	30.2	31.5	23.8	24.4	24.0	19.6–41.6	26.35
$CaCl_2$	47.2	36.7	34.1	30.9	35.5	33.0	35.4	38.2	43.4	35.4	32.0	37.4	30.9–47.2	36.60
$CaBr_2$	50.5	41.1	40.0	37.9	42.4	41.3	45.1	46.3	48.7	42.3	38.3	45.3	37.9–50.5	43.27
$SrCl_2$	44.4	33.8	31.5	29.1	33.0	33.4	33.7	36.2	40.3	33.3	31.1	34.2	29.1–44.4	34.50
$BaCl_2$	39.3	26.5	25.6	30.0	32.5	33.0	35.5	38.7	40.3	33.5	31.4	34.9	25.6–40.3	33.42
$ZnSO_4$	21.1	15.6	14.1	13.9	15.6	15.8	17.2	18.5	20.7	15.9	15.2	16.9	13.9–21.1	16.71
$Al_2(SO_4)_3$	23.0	14.7	14.8	14.2	17.3	16.0	17.5	18.5	20.3	15.3	15.1	16.1	14.2–23.0	16.90
Average of salts	37.71	26.51	25.66	23.45	26.41	27.39	29.81	31.24	34.11	27.82	25.62	28.63		

peptization is increased. Such results should work in opposite directions, and nullify the correlation which exists in the 1.0 *N* series.

The high negative coefficients of correlation for the 1.0 *N* series indicate that the nitrogen extracted by the salt solution does not contribute to the protein which is involved in forming the gluten structure of the loaf. While

TABLE 3.—*Coefficients of Correlation between Loaf Volume and Per Cent Protein Extracted by N/1 Salt Solutions.*

Salt		Salt	
Li acetate	$r = -0.702 \pm 0.099$	K_2 tartarate	$r = -0.695 \pm 0.101$
LiCl	$r = -0.760 \pm 0.082$	$MgCl_2$	$r = -0.836 \pm 0.059$
NaCl	$r = -0.757 \pm 0.083$	$MgBr_2$	$r = -0.731 \pm 0.091$
Na_2SO_4	$r = -0.771 \pm 0.079$	$MgSO_4$	$r = -0.925 \pm 0.028$
Na_3 citrate *	$r = -0.788 \pm 0.077$	$CaCl_2$	$r = -0.796 \pm 0.071$
Na_2HPO_4	$r = -0.726 \pm 0.092$	$CaBr_2$	$r = -0.817 \pm 0.065$
KF	$r = -0.834 \pm 0.059$	$SrCl_2$	$r = -0.774 \pm 0.078$
KCl	$r = -0.794 \pm 0.071$	$BaCl_2$	$r = -0.583 \pm 0.128$
KBr	$r = -0.828 \pm 0.061$	$ZnSO_4$	$r = -0.768 \pm 0.080$
KI	$r = -0.672 \pm 0.107$	$Al_2(SO_4)_3$	$r = -0.704 \pm 0.098$
K_2SO_4	$r = -0.773 \pm 0.078$		

Average of all (21) salts (1.0 *N*)	$r = -0.798 \pm 0.071$
Average of all (18) salts (0.5 *N*)	$r = -0.785 \pm 0.078$
Average of all (15) salts (2.0 *N*)	$r = +0.323 \pm 0.136$
K_2SO_4 (5 per cent)	$r = -0.797 \pm 0.071$

* n = 11.

these coefficients of correlation are negative and accordingly might be taken as indicating that the peptizable fraction actually depressed the loaf volume, it should be remembered that coefficients of correlation of the same magnitude but of opposite sign would have resulted, if the calculations had been made between loaf volume and per cent of protein not peptized by the salt solution. Probably this would more nearly represent the situation, i.e., there is a higher positive correlation between that fraction of the protein which is not peptized by salt solutions and the loaf volume than there is between total protein and loaf volume,* and the fraction of the protein which is peptized by the salt solution plays little or no rôle in the processes which can be measured by loaf volume.

After the above correlations had been calculated, a search was made for other data from which similar coefficients of correlation could be computed. Rumsey (**1922**), Collatz (**1922**), and Sharp and Gortner (**1923b**) made a series of studies on another series of flours which, in the course of the investigations, were baked a number of times so that the loaf volume may be regarded as having a satisfactory degree of accuracy. Sharp and Gortner (**1923b**) report in their Table 22 the loaf volume and the per cent of protein soluble in 5 per cent K_2SO_4 solution. Recalculating these latter figures into per cent of total protein soluble in 5 per cent K_2SO_4 and using these data to calculate the coefficient of correlation, there was found the relationship between per cent of protein soluble in 5 per cent K_2SO_4 solution and loaf volume (N = 11) of $r = -0.824 \pm 0.065$, which is in very satisfactory agreement with the value of $r = -0.797 \pm 0.074$ in the Gortner, Hoffman, and Sinclair series. Accordingly both the flours used by Collatz, Rumsey, and Sharp, and those used by Grewe and Bailey, and Gortner, Hoffman, and Sinclair show complete and independent agreement. Sharp and Gortner (**1923b**) did not recog-

* The coefficient of correlation between total protein and loaf volume for the present series of flours (N = 12) was $+0.539 \pm 0.138$.

nize this relationship in their series of flours, because of the fact that the potassium-sulfate-soluble protein was calculated as per cent of the total flour and not as per cent of the protein which was present in the flour. Consequently they overlooked one of the most striking features of their data.

A search of the literature for data suitable for additional calculations was not very successful. In most instances either the loaf volume or the per cent of total protein or the per cent of protein soluble in 5 per cent K_2SO_4 were lacking. Again it is fairly well recognized that there is a high probable error attached to the value of a single bake, this error being so great that one hesitates to use loaf volumes unless they represent the averages of several bakings.

However, Whitcomb and Sharp (**1926**), and Sharp (**1926a**) present some interesting data on wheats harvested at various stages of maturity and on wheats frozen and harvested at various stages of maturity. This set of data is of interest because of the fact that all samples were of the same variety (Marquis) and grown under the same soil and climatic environment, the only variables being age of kernel and frozen or non-frozen. They report three sets of bakes from the resulting flours. Believing that the average of the three bakes is more truly representative of the loaf volume, the average loaf volumes were taken for calculations. The coefficients of correlation of their data showed a coefficient of correlation between loaf volume and per cent of protein extracted by 5 per cent K_2SO_4 for all samples [both frozen and non-frozen, their Nos. 135-155, inclusive ($N = 18$)] of $r = -0.880 \pm 0.036$. The similar correlation for non-frozen samples only ($N = 10$) was $r = -0.646 \pm 0.124$, and for frozen samples only ($N = 8$) $r = -0.976 \pm 0.011$.

Of course, there is nothing new in the observation that excessively large proportions of the protein of immature and frosted wheat are peptizable by 5 per cent K_2SO_4 solutions. Neither is it a new observation that such wheats produce low loaf volume. Nevertheless, the coefficient of correlation between the potassium-sulfate-soluble protein and the loaf volume of the frosted wheats is so nearly unity as to suggest a causal relationship and to indicate that the salt-peptizable portion of the protein was contributing nothing to the loaf volume.

It is highly probable that we shall in the future find groups of wheat samples where little or no correlation exists between the loaf volume and the per cent of protein peptizable by salt solutions. In such a case we must conclude either of two alternatives, (1) that there is present in such samples an adequate amount of good protein to provide the maximum loaf which can be provided under the conditions of the bake and that the variability in loaf volume is controlled by other factors, such as saccharogenic activity, etc., or (2) that the salt-peptizable protein may in certain instances contribute to the loaf volume.

The latter alternative is not inconsistent with colloidal theory. We know nothing in regard to the relative size of the protein aggregates which are peptizable by the salt solution. It may well be that in certain wheats and under certain conditions the breakdown (or the non-formation) of the gluten proteins halts just at the border of gluten particle size. In other instances it may represent a rather profound degradation. Aggregates of the former may well favor a larger loaf volume; the highly degradated protein may be inert or actually decrease the volume. In any event, the observations so far recorded are consistent, and indicate that where one is dealing with (a) damaged or immature wheats, or (b) a series of wheat flours representing various types and varieties of wheat grown under different environmental conditions, data

of value can be obtained by ascertaining how large a proportion of the total protein can be peptized by a salt solution.

As already indicated the great variability in the proportion of protein peptized by the various salt solutions in their various concentrations raises many problems of protein chemistry. It is no longer adequate to consider the salt-soluble fraction as a mixture of albumins and globulins, for the cited studies prove that such is not the case. The high values for non-gluten protein peptized by KI solutions, for example (266 to 391 per cent) show conclusively that either the gliadin or the glutenin (or both) differ from flour to flour in their colloidal behavior, as evidenced by ease of peptization. However, while colloid-chemical differences have been demonstrated, the cause and nature of such differences are problems for future research.

The Starch.*

While the literature is replete with investigations which deal with the colloidal and chemical properties of the wheat and wheat flour, relatively little attention has been devoted to the starch, although it comprises the bulk of the flour. There are, however, a few recent papers which may denote an awakening interest in this important constituent.

Rask and Alsberg (**1924**) studied the viscosity of gelatinized wheat starches from a number of wheats. They used the Stormer viscosimeter and concentrations of starch pastes ranging from 3 to 6 per cent. They found that viscosity could be expressed by the equation,

$$\log \text{viscosity} = \log b + aC,$$

where a and b are constants and C is the concentration of the starch in the gelatinized paste. Insofar as the different starches are concerned, they found that, in general, the gelatinized starch pastes from winter wheats gave a higher viscosity than the pastes from spring wheats, and they note that high starch-paste viscosity is associated with two or more of the following conditions in the case of each flour, (1) low loaf volume, (2) low protein content, (3) high temperature during the growing period; and that starch pastes showing low viscosity are associated with the opposite condition.

In a study of the temperature of gelatinization of wheat starch using viscosity methods, Alsberg and Rask (**1924**) find that this is not a fixed point but that gelatinization occurs over a rather wide temperature range which may be as much as 25° or 30°.

Hermano and Rask (**1926**) investigated a variety of wheat starches with especial reference to their ease of hydrolysis by saccharogenic enzymes, and confirm the viscometric formula proposed by Alsberg and Rask, and further show that gelatinized wheat starches may vary greatly in viscosity at equivalent concentrations. They note, however, that while these same starches differed considerably in the ease with which they were hydrolyzed by amylase, there was no apparent relationship between the viscosity of gelatinized starches and the rate of hydrolysis by amylase.

The Preparation and Fermentation of the Dough Batch.

One of the strongest arguments in favor of a colloidal view of flour strength as residing in the proteins lies in the observations of Sharp, Gortner, and Johnson (**1923**), which were later confirmed by Johnson (**1928**), that if

* *See* paper on Starch by M. Samec in Vol. IV of this series. J. A.

a flour is doughed up with 70 or 95 per cent alcohol and the alcohol immediately evaporated at room temperature, the ability of the flour to form gluten and to produce a satisfactory loaf of bread is destroyed. It had earlier been "proven" that gliadin was essential for bread manufacture, since when gliadin was removed by extracting the flour with alcohol (70 per cent), the bread-making properties were destroyed. In the experiments of Sharp, Gortner, and Johnson nothing was added to the flour nor was anything removed from the flour; nevertheless the desirable bread-making properties were to a large extent destroyed, and coincident with this destruction there was a sharp decrease in the maximum viscosity which could be attained by the addition of lactic acid. These experiments indicate that protein hydration and swelling as measured by viscosity changes may involve purely colloidal properties which cannot be ascribed to stoichiometrical chemical reactions.

The manufacture of bread involves many colloidal processes. The "absorption" of a flour, or the amount of water which it is necessary to add to form a dough of satisfactory consistency, is determined by the surface area of the starch particles and by the hydrophilic properties of the gluten proteins. The salts which are added play a rôle in the hydration of the gluten colloids and probably tend to "tighten" the gluten and increase its gas-holding capacity. This is particularly true of salts with bivalent ions. It is a matter of common knowledge among bakers that a saturated solution of calcium sulfate will "tighten up" the gluten of a weak flour. Bailey and Weigley (**1922**) have shown that weak-flour doughs are much more permeable to carbon dioxide than are similar doughs from strong flour. The gluten-starch gel is less coherent and breaks apart more readily under the tension of the carbon dioxide produced by the yeast fermentation. Certain of the "flour improvers" which are upon the market probably owe their beneficial properties, at least in part, to their action upon the gluten colloids, in that they increase the tenacity with which gluten particle adheres to gluten particle in the dough gel.

Fermentation.

Bailey and Johnson (**1924**) and Johnson and Bailey (**1925**) introduced a new technic for measuring the colloidal properties of a dough during fermentation. They followed the ratio of carbon dioxide retention to carbon dioxide loss from the fermenting dough mass and show that during the early portion of the fermentation period carbon dioxide production by the yeast fermentation greatly exceeds the carbon dioxide loss from the dough. After fermentation has progressed for some time, there is a rapid increase in the loss of carbon dioxide from the fermenting mass which can be ascribed to the rupture of gluten membranes by the pressure of carbon dioxide in the fermenting dough. The strong flours show a gas-retaining capacity which is much greater than that shown by weak flours. Rye flour doughs have a low gas-retaining capacity, although the rate of gas production in the dough is high. The inferior gas-retaining capacity of the rye flour appears to be responsible for the dense, compact loaves which rye flour ordinarily yields.

Sharp and Gortner (**1924**), in a study of the effect of yeast fermentation on the imbibitional properties of glutenin report that the viscosity of a washed wheat flour-water suspension is markedly increased to a maximum by yeast fermentation and that at a longer fermentation the viscosity again falls off.

Johnson (**1928**) points out that bread of better texture, color, and volume is produced from flours from which the ether-soluble materials have been extracted than from natural flour, and that the loaf volume of low-grade flours

is increased to a greater extent than is the loaf volume from patent flours. He confirms the observation of Sharp, Gortner, and Johnson (**1923**) that treatment of flour with 70 or with 95 per cent alcohol reduces the loaf volume, and reports that such treatment likewise reduces the viscosity of leached and acidulated flour-water suspensions and also reduces the extensibility as measured by the Chopin extensimeter.

During fermentation the hydrogen-ion concentration in the dough increases (Bailey and Sherwood, **1923**). This increase has its effect not only upon the yeast and the flour enzymes but also upon the gluten colloids in that it alters to some extent their state of hydration. It is probable, however, that the beneficial action of the increased hydrogen-ion concentration is, in a large measure, due to its effect upon the yeast and flour enzymes so that the carbon dioxide production in a unit of time is greatly increased and a high ratio of $\frac{CO_2 \text{ production}}{CO_2 \text{ diffusing through the gel}}$ is maintained. Certain of the flour improvers contain salts, e.g., NH_4Cl, which contribute an increased hydrogen-ion concentration due probably to the yeast utilizing the ammonium ion and forming hydrochloric acid (*cf.* Bailey and Sherwood, **1923**).

If the colloidal properties of wheat gluten are responsible for the retention of the carbon dioxide in the dough during the fermentation and the initial portion of the baking period, one should expect the greatest retentivity to occur when the gluten proteins are at or near their isoelectric point. This hypothesis has been tested by Grewe and Bailey (**1927a**) in an experiment where a series of doughs were kept during the fermentation period at hydrogen-ion concentrations ranging from pH 6.5 to pH 8.0, and where the final bread had a pH of 6.0 to 6.6. The largest loaf volumes were obtained from doughs having a pH of 7.5 to 8.0, and the texture of these breads was very satisfactory. The best texture was obtained where the dough had a pH of 7.0 and the finished bread a pH of 6.2. Grewe and Bailey believe that the only advantage of allowing the hydrogen-ion concentration to increase during the fermentation period is that such an increase brings about increased activity of the saccharogenic enzymes.

The Baked Product.

In the baking process, the proteins of the gluten-starch gel are largely irreversibly coagulated by the high temperature and a part of the starch grains are ruptured, changing them from essentially a lyophobic colloid system to a highly hydrophilic system. The excess of moisture existing in the dough is thus "bound" by the hydrophilic colloids, and a relatively dry protein-starch gel is formed which we familiarly call a loaf of bread. This system likewise shows pronounced colloidal properties. Boussingault (**1852**) concluded that the staling of bread was not due to water evaporating from the loaf but that if a stale loaf was heated to 70° C. it became in every respect like fresh bread.

Katz, in a series of papers (**1912, 1912a, 1915**), found that in becoming stale, the crust gains 8 to 9 per cent of water and the crumb loses 1 to 2 per cent. He later showed that when bread is stored at temperatures ranging from 50° to 90° C., it remains fresh indefinitely if bacterial interference is prevented. At very low temperatures it does not stale, and he suggested that the change occurs in the starch grains and not in the protein. Lorenz (**1913, 1913a**) concluded that staling is not due to a loss of water, which often does not exceed 2 per cent, but that gelatinized starch is metastable and passes over into other forms at certain temperatures. He found that the stale form was

stable from —80° to +60° C. and that heating this form to 80° C. in a tight chamber changed it back to the fresh form again. He pointed out that at ordinary temperatures the stale form is the stable form and that the hydrated starch granules lose water to the protein in becoming stale.

Other workers have reached similar conclusions. Whymper (**1919, 1920**) believes that reversion of the gelatinized starch is primarily responsible for staling. He states (**1919**), "Staleness may be attributed to (I) deposition of solid starch in the crumb of bread starting between six hours' and twenty-four hours' cooling period (a) by change in temperature (b) accelerated by the presence of solid starch particles already existing in the crumb. (II) Partial polymerization of starch independent of the deposition already stated which tends to crumble the gelatinous nature of the bread crumb when fresh." This last statement may be restated in colloid terminology as an alteration in the gel structure of the loaf. We have, therefore, in the staling of bread changes within a colloidal gel system involving differential syneresis and imbibition among the various components in the gel. Certain of the colloidal aspects of this phenomenon require further investigation.

Dunn and Bailey (**1928**) have made a physico-chemical study of factors involved in the checking or fracture of baked products similar to the English hard-sweet biscuit. On the assumption that the biscuit dough may be regarded as a colloid gel and that the baked biscuit may be regarded as a more or less dehydrated gel in which there is an unequal distribution of the water, they note that the moisture content of the biscuit dough as it enters the oven may vary from 10 to 40 per cent and that during the process of baking this material undergoes several important changes. The gluten of the flour is coagulated by heat and converted from an elastic substance into one which is more or less rigid during this process, losing part of its capacity to hold water. On the other hand, the starch in the raw state absorbs comparatively little water but in the baking process is gelatinized, takes on water, and assumes a jelly-like consistency. As the baking time is increased, both the coagulated gluten and gelatinized starch lose water, but all parts of the biscuit do not lose water at the same rate, the rim or periphery tending to be drier than the central or interior portions of the baked product. When the biscuit leaves the oven it has a given moisture content, but the various parts of the biscuit are not in equilibrium, so that the drier portions tend to absorb water from the more moist portions. Accordingly, the central portion of the biscuit, losing water, should tend to shrink in size, whereas the rim or drier portion, absorbing water, should tend to swell, and in this rigid gel the opposing forces of shrinking and swelling cause checking or the fracture of the baked product. These authors devised a unique method of following the changes involved in this rearrangement of the moisture gradient. Tiny fragments of steel were embedded in the biscuit dough from which biscuits were baked. Photographs of the baked biscuit were then taken under X-rays, thus giving the distribution of the metallic fragments throughout the fresh biscuit matrix. A reference disk of invar on the photographic plate provided for subsequent measurements of relative expansion or shrinkage. They note that the warm biscuit is a plastic system, rigidity rapidly increasing as cooling takes place. X-ray studies of the biscuit taken at intervals showed a displacement of the metallic fragments in the various portions of the biscuit and definitely proved a shrinkage of the gel structure on the interior and an expansion due to the absorption of moisture in the periphery or rim, thus setting up strains which caused a rupture of the baked product. They recommend that the freshly baked product be allowed to cool in an atmosphere where the relative humidity is

such as to allow the rim to take up moisture from the air rather than from the central portion, so as to avoid strain in the baked product. In this way the loss due to checking can be almost entirely eliminated. Biscuits which were baked for six minutes, when aged at a relative humidity of 20 per cent, showed 70 per cent of checked product, whereas duplicate samples aged for forty-eight hours at a relative humidity of 40 per cent showed no checked biscuit.

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INDEX TO AUTHORS *

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